Acquisition Directorate

Research & Development Center

Report No. CG-D-03-16

Mitigation of Oil in Water Column: Concept Development

Distribution Statement A: Approved for public release. Distribution is unlimited.

This study was funded in part by the U.S. Department of the Interior, Bureau of Safety and Environmental Enforcement (BSEE) through Interagency Agreement E14PG00028 with the United States Coast Guard Research and Development Center.

June 2016

Homeland Security

N O T I C E

Mr. James E. Fletcher
Environment &Waterways Branch Chief
United States Coast Guard
Research & Development Center
1 Chelsea Street
New London, CT 06320

Technical Report Documentation Page

1. Report No. CG-D-03-16	2. Government Accession Number	3. Recipient's Catalog No.
4. Title and Subtitle Mitigation of Oil in Water Column: Concept Development		5. Report Date June 2016
		6. Performing Organization Code Project No. 4702
7. Author(s) Alexander Balsley, Dr. Michele Fitzpatrick, Peter A. Tebeau		8. Performing Report No. RDC UDI # 1291
9. Performing Organization Name and Address Shearwater Systems, LLC Contractor for USCG Research and Development Center 1 Chelsea Street New London, CT 06320	U.S. Coast Guard Research and Development Center 1 Chelsea Street New London, CT 06320	10. Work Unit No. (TRAIS)
		11. Contract or Grant No. Task Order #HSCG32-16-J-500015
12. Sponsoring Organization Name and Address COMMANDANT (CG-MER-3) ATTN: INDUSTRY & INTERAGENCY COORDINATION DIVISION US COAST GUARD STOP 7516 2703 MARTIN LUTHER KING JR AVE SE WASHINGTON DC 20593-7516	OIL SPILL RESPONSE DIVISION, BSEE ATTN: Ms. KRISTI MCKINNEY 381 ELDEN STREET, HE 3327 HERNDON, VA 20170	13. Type of Report & Period Covered Final
		14. Sponsoring Agency Code Commandant (CG-MER-3) US Coast Guard Washington, DC 20593
15. Supplementary Notes The R&D Center's technical point of contact is Alexander Balsley, 860-865-0474, email: Alexander.Balsley@uscg.mil		

16. Abstract (MAXIMUM 200 WORDS)

This report summarizes the results of Phase II-A (Concept Development) of an RDC effort to develop a system that can mitigate the impacts of oil in the water column on the surrounding environment through containment or removal of the submerged oil. This phase of the project involved demonstrating the technical and scientific basis of two approaches as well as their feasibility. Argonne National Laboratory (ANL) proposes to use polyurethane foam, a commonly used material for many general purposes, as the material of choice to adsorb submerged oil. Prior to use, the foam undergoes a series of chemical processes in order to render it oleophilic and thus more susceptible to adsorbing and retaining oil droplets and dissolved oil in the water column. Dynaflow, Inc. is developing a mitigation system that utilizes a number of microbubble generators to be placed beneath a submerged oil plume in order to allow air bubbles of differing sizes to adhere and lift oil droplets in the water column to the surface where it can be removed by traditional oil recovery methods. Dynaflow is also developing fast-running computer software to optimize the position and number of generators and predict the oil recovery location. The RDC evaluated Phase II-A findings and determined that vendor-specific recommendations have potential for successful outcomes in Phase II-B (Prototype Development and Demonstration). Overall, the RDC recommends that both vendors move forward to Phase II-B.

This study was funded in part by the U.S. Department of the Interior, Bureau of Safety and Environmental Enforcement (BSEE) through Interagency Agreement E14PG00028 with the United States Coast Guard Research and Development Center.

17. Key Words Adsorbent Foam, Adhesion, Microbubble, Sinking Oil, Submerged Oil, Oil Mitigation, Sorbent, Water Column	18. Distribution Statement Distribution Statement A: Approved for public release. Distribution is unlimited.		
19. Security Class (This Report) UNCLAS//Public	20. Security Class (This Page) UNCLAS//Public	21. No of Pages 60	22. Price

(This page intentionally left blank.)

EXECUTIVE SUMMARY

The U.S. Coast Guard Research and Development Center (RDC) is undertaking an R&D effort to identify and develop a system that can mitigate the impacts of oil in the water column on the surrounding environment through containment or removal of the submerged oil. This report summarizes the results of Phase II-A (Concept Development) of the effort in which developers were solicited through a Broad Agency Announcement (BAA) to develop a proof-of-concept of their mitigation systems. This effort is a part of the overall Research and Development (R&D) effort to advance response technology for varying types of oil spills. This subtask addressing entrained oil mitigation is similar in scope and objective to the previous effort to detect subsurface oil in near-shore and river environments (Fitzpatrick et al., 2014).

In the BAA, vendors were directed to address a number of capabilities and attributes in describing and conducting preliminary laboratory testing of their concepts. Four contractors responded with descriptions of their mitigation systems and their planned developmental activities. From the four proposals, two mitigation technologies were chosen for further development: foam adsorption and microbubble flotation.

Argonne National Laboratory (ANL) proposes to use polyurethane foam, a commonly used material for many general purposes, as the material of choice to adsorb submerged oil. Prior to use, the foam undergoes a series of chemical processes in order to render it oleophilic and thus more susceptible to adsorbing and retaining oil droplets and dissolved oil in the water column.

Dynaflow, Inc. is developing a mitigation system that utilizes a number of microbubble generators to be placed beneath a submerged oil plume in order to allow air bubbles of differing sizes to adhere and lift oil droplets in the water column to the surface where it can be removed by traditional oil recovery methods. The team is also developing fast-running computer software to optimize the position and number of generators and predict the oil recovery location.

Specific capabilities of each system with respect to each of the performance criteria in the BAA are summarized in a table in Section 2.4 of this report. An overall assessment of the current capabilities of each system and potential for further development and demonstration is provided in Section 3.0.

(This page intentionally left blank.)

TABLE OF CONTENTS

TABLE OF CONTENTS (CONTINUED)

LIST OF FIGURES

LIST OF TABLES

(This page intentionally left blank.)

LIST OF ACRONYMS, ABBREVIATIONS, AND SYMBOLS

ALD	Atomic layer deposition
ANL	Argonne National Laboratory
ANS	Alaska North Slope
API	American Petroleum Institute
ASTM	American Society for Testing and Materials
BAA	Broad Agency Announcement
BSEE	Bureau of Safety and Environmental Enforcement
cm	Centimeter (10^{-2} meters)
CRRC	Coastal Research and Response Center
CTD	Conductivity, temperature, and depth
ft	Foot or feet
g	Gram(s)
gal	Gallon(s)
gpm	Gallons per minute
GPS	Global Positioning System
kt	Knot(s)
L	Liter(s)
µm	Micron(s) or micrometer(s) (10^{-6} meters)
m	Meter(s)
M/T	Motor tanker
min	Minute(s)
NIC	National Incident Commander
nm	Nanometer(s) (10^{-9} meters)
No.	Number
NOAA	National Oceanographic and Atmospheric Administration
NRC	National Research Council
Ohmsett	National Oil Spill Response Research and Renewable Energy Test Facility
OPA 90	Oil Pollution Act of 1990
OSAT	Operational Science Advisory Team
ppt	Parts per thousand
R&D	Research and Development
RDC	USCG Research and Development Center
SIS	Sequential infiltration synthesis
T/B	Tank barge
T/V	Tanker vessel
TMA	Trimethyl aluminum
UAC	Unified Area Command

LIST OF ACRONYMS, ABBREVIATIONS, AND SYMBOLS (CONTINUED)

USCG	United States Coast Guard
V-SORS	Vessel-Submerged Oil Recovery System
WCSS	Western Canada Spill Services

1 INTRODUCTION

A challenge that the U.S. Coast Guard (USCG) faces in many oil spills, including the Deepwater Horizon oil spill response in 2010, is the inability to determine the location of subsurface oil plumes in near-real time, which inhibits timely decisions to protect the environment, numerous water-intakes, and commercial facilities. Other issues that negatively impacted the response included poor visibility in deeper waters, difficulty in tracking oil movements in fast-moving currents, and an inability to discover very low levels of oil or dispersed oil at all depths. From 2011 to 2013, the Coast Guard Research and Development Center (RDC) worked to close these gaps by advancing the technology for detecting subsurface oil in near-shore and river environments.

Two prototype detection systems were demonstrated at the National Oil Spill Response Research and Renewable Energy Test Facility (Ohmsett) in Leonardo, NJ for their feasibility and performance. They are based on two different technologies: sonar and optical technology. The Wide Band Multibeam Sonar developed by Norbit consists of lightweight equipment that has the ability to provide a 3D topology of the oil plume. It also has integrated processing capabilities and can be mounted on many types of surfaces. WET Labs provided an optical tool using the wide-angle-scattering inversion method with a fluorometer providing backup verification of hydrocarbon presence in the water column. It measures refracted and reflected light off of suspended particles to determine the droplet size distribution and viscosity of oil based on their distinct scattering angles. The inversion methods are used to identify and quantify suspended oil emulsions. Both systems are portable and can be deployed easily by one or two persons. See Fitzpatrick et al. (2014) for details on the detection system development and demonstration.

With the detection phase (Phase I) of RDC's Detection and Mitigation of Oil in the Water Column project completed, the focus of the RDC shifted to mitigation (Phase II). This portion of the project builds on the efforts and lessons learned during RDC's work in Phase I as well as those learned during the Deepwater Horizon response. Once submerged oil in the near-shore or river environments has been encountered, the next step is to make the decision of whether an active approach is necessary to remove the oil or mitigate the subsurface plume's impacts on the environment, water intakes, and commercial facilities. Currently there is no well-established technology, technique, or strategy to prevent the detected submerged oil from having further adverse impacts on the environment or manmade structures.

1.1 Objective

The RDC is undertaking a Research and Development (R&D) effort to identify and develop a system that can mitigate the impacts of oil in the water column on the surrounding environment through containment, diversion, or removal of the submerged oil. It is a part of a larger effort in the USCG R&D program to develop countermeasures and cleanup technologies for a range of oil spills.

Submerged oil is defined as neutrally buoyant oil (with or without sediment particles attached) suspended in the water column. The Deepwater Horizon wellhead released large quantities of submerged oil that remained below the water surface and presented numerous challenges to oil spill responders. However, the scope of this project is limited to near-shore environments up to a depth of 200 feet (ft) (61 meters (m)), which is where the majority of oil spills in the nation's waterways occurs.

This report summarizes the results of Phase II-A (Concept Development) efforts in which contractors were solicited through a Broad Agency Announcement (BAA) to develop a proof-of-concept of their mitigation systems. Phase II-A included the concept development of a technology, technique, or strategy that mitigates a subsurface oil plume's impacts on the environment, water-intakes, and commercial facilities through containment, diversion, or removal. White papers and subsequent proposals needed to demonstrate the technical and scientific basis of their approaches as well as their feasibility. Four contractors responded with descriptions of their mitigation systems and their planned developmental activities. Two were selected for further work. In this report, these results are evaluated to determine recommendations for Phase II-B (Prototype Development and Demonstration).

1.2 Background

The Oil Pollution Act of 1990 (OPA 90) requires that Federal agencies conduct a coordinated research program, in cooperation with academic institutions and private industry, to improve the nation's capability to detect, monitor, and conduct countermeasures, cleanup, and remediation operations to respond to accidental oil spills. Responding to oil spills on the surface of the water is often a difficult task with recovery rates generally averaging about 20 percent or less of the oil spilled. Responding to spills of submerged oil is far more complex due to the problems associated with operating in an underwater environment where oil is spreading and dispersing in three-dimensions, visibility is limited, deploying divers is dangerous, and recovery equipment must be far more robust and complex than that used on the surface. However, a number of recent spills involving heavier oils that sank below the surface, as well as the subsurface oil encountered in the Deepwater Horizon spill, underscore the need for improving technology for subsurface oil spill response. A summary of the problems and technologies associated with submerged oil is provided below. Additional information can be found in Appendix A. See National Research Council (NRC) (1999) and Michel (2006) for more details.

1.2.1 Oil in the Water Column

The term submerged oil generally refers to any oil that is not floating on the surface. In an oil spill involving submerged oil, three location scenarios are possible :

- *Overwashed*: thicker oil that is floating near the water surface but is covered by a layer of water due to wave action. This can obscure the oil slick from visual monitoring and remote sensing at the surface.
- *Suspended*: oil globules or droplets that are neutrally buoyant at depth and move in the water column under the influence of currents.
- *Sunken*: oil that is negatively buoyant and rests on the bottom of the water body.

Spilled oil can be suspended in the water column in roughly four distinct scenarios. The physical and chemical properties of oil resulting from these scenarios can be very different and change with time.

- Heavy oil from a surface spill that tends to sink under certain conditions, and is generally called suspended oil while it is in the water column and sunken oil when it reached the sea bottom.
- Oil rising to the surface from a subsea blowout.
- Fine droplets of oil resulting from chemical dispersants being applied to either a surface spill or subsea blowout or due to natural dispersion.

- Fast current water that can move oil and sediment quickly and not permit the oil to surface or sink to the bottom.

As described by the NRC (1999) and Michel (2006), each of the above scenarios presents its own challenges depending on the location and condition of the oil. This is particularly true when attempting to detect, identify, characterize, and mitigate oil that is suspended in the water column.

1.2.2 Oil in Water Column Mitigation Techniques

The selection of mitigation techniques is highly dependent on the specific location and environmental conditions during the oil spill, the characteristics of the oil and its state of weathering and interaction with sediments, the availability of equipment, and logistical support for the cleanup operation. Further complications include the difficulty in detecting and tracking the oil from the surface in real time and the movement and dispersion of the oil in three dimensions. In addition, the potential environmental impacts of implementing these methods, particularly in sensitive benthic habitats, must be considered.

The effectiveness of mitigation technologies is heavily dependent on the condition of the oil suspended in the water column. Most of the technologies recommended in the literature and used in past spills apply to larger fragments of very viscous oil (often termed globules, tarballs, or pancakes). The technologies recommended for mitigation of heavy and/or viscous oil are listed below. Details of these technologies can be found in Appendix A. Descriptions of selected Case Studies can be found in Appendix B.

1.2.2.1 *Mitigation of Suspended Oil Droplets*

Oil droplets can be suspended in the water column if their size and composition render them neutrally buoyant, or environmental conditions keep droplets below the surface that would normally rise due to their buoyancy. Following the *SS Arrow* spill of Bunker C oil, researchers found oil particles in the water column ranging from 5 to 2,000 microns (µm) for months following the spill (Forrester, 1971).

While there is no readily available information in the literature about mitigation of suspended oil droplets in actual spills, mitigation technologies that may apply include deep draft oil booms, silt curtains (for larger droplets, depending on the design of the curtain), sorbents, and pneumatic barriers (or bubblers).

Deep draft oil booms. Under certain conditions, booms with a deep draft may contain some of the suspended oil. A deep draft would be considered greater than about 4 feet (ft) (1.2 meters (m))In general, deep draft oil booms are successful for water column oil containment only when the oil remains in the upper water column, the currents are low, and the waves are small.

Silt Curtains. Silt curtains, which are normally used to control the transport of suspended sediment during dredging operations, are typically restricted to water depths of 10-20 ft (3-6 m) and are deployed so that the bottom of the curtain does not extend to the seabed.

Sorbents. Sorbent materials in the form of pom-poms, snare nets, and the Vessel-Submerged Oil Recovery System (V-SORS) are often used for detection of submerged oil (see Appendix A for pictures and additional information). They are also recommended as recovery technologies in some situations, primarily for viscous oil.

Pneumatic Barriers. Pneumatic barriers, also known as bubblers, involve injecting air at the seabed and forming a bubble plume that rises to the surface. They were originally designed to collect and/or divert oil at the surface. Pneumatic barriers have also been considered for protecting sensitive structures such as seawater intakes and marinas against oil suspended in the water column, and one was used at the Lake Wabamun spill at one of the power plant water intake canals (Fingas, 2011), but little data is available for assessing their performance. Their optimal application is in confined areas in shallow water (less than approximately 6.5 ft or 2 m (Chapman, 2012)).

1.2.2.2 *Mitigation of Submerged Viscous Oil*

In addition to the silt curtains, sorbents, and bubblers described above, the following methods are recommended for potential mitigation of heavy oil suspended in the water column.

Nets and Trawls. Midwater trawls and nets may be used for containing heavy oil in certain conditions. The performance of these systems depends on the viscosity of the oil and being able to locate and concentrate the oil. In addition to containing dispersed oil, nets and trawls can also be used as collection devices (Brown and Goodman, 1987; Delvigne, 1987), and are often combined with sorbents for this purpose. Some disadvantages to nets and trawls are they are labor intensive and slow. Nets can fail from excess accumulation of heavy oil and debris.

Manual Removal. The manual removal of oil, one of the most widely used recovery methods for viscous oil, involves divers or boat-based personnel using dip nets or seines to collect oil, which is temporarily stored in bags or containers. The biggest disadvantages of manual removal are the large manpower and logistical requirements, slow rates of recovery, strong dependency on favorable weather conditions, and the potential for the oil to be transported while it is being recovered.

1.3 Approach

1.3.1 Contracting Approach

The RDC developed qualities that an oil mitigation technology should minimize or maximize and included them in a BAA that was released in October 2014. It called for a two-phased approach to the mitigation of oil within the water column. The scope of the BAA included Phase II-A (Concept Development) and a Government Option for Phase II-B (Prototype Development and Demonstration). The Government Option allows the Government to make a decision whether or not to move ahead into the next phase depending on a number of factors, including feasibility of technical approach, importance to agency programs, and fund availability.

The RDC received four responses and selected two ideas for Phase II-A proof-of-concept development and preliminary testing. The selected contractors and their projects chosen were:

- Argonne National Laboratory’s Adsorbent Foam
- Dynaflow Inc.’s Microbubble Oil Flotation System

1.3.2 Performance/Capability Requirements

The BAA required the contractor to develop a design concept for an oil mitigation system prototype. It also further specified that the design concept minimize/maximize or demonstrate as many of the following capabilities as possible:

1. Extent of oil mitigation or removal rates and quantities;
2. Types of oil mitigated (e.g., droplets, tarballs, dissolved oil);
3. Minimization of environmental impacts with a focus on wildlife and plant life;
4. Effective limits in terms of depth of oil and deployment;
5. Effective limits in terms of environmental conditions such as current, wave height, winds, day/night, inclement weather, etc.;
6. Ease of use to include deployability and recovery of equipment;
7. Transportability;
8. Operability in fresh/seawater;
9. Ability to observe and monitor subsurface oil collection;
10. Reusability; and
11. Safety to personnel deploying and recovering.

2 DESIGN CONCEPT DESCRIPTIONS

2.1 Technology Overview

The design concepts presented here represent two distinct mitigation technologies, foam adsorption and microbubble flotation.

2.1.1 Argonne National Laboratory Foam Adsorption

Sorbent technologies such as V-SORS, sorbent drops, and snare nets are currently the most popular techniques recommended for detection and mitigation of submerged and sunken oil (see Appendix A for examples). They have been used in many spills of heavy oil, sometimes successfully, sometimes not. The technology proposed by Argonne National Laboratory (ANL) is a new application of this technology and would apply to suspended oil droplets and dissolved oil.

Oil suspended in the water column can include droplets, globules of oil and emulsified oil, and tarballs, which are globules of heavily weathered oil. The oil will be found in varying dimensions and viscosities, such that one containment and recovery configuration may not capture all the suspended oil. The ANL concept of sorbent material is designed to capture small droplets or dissolved oil and will be integrated into a net for trawling. The material is designed to be reused by feeding through compression rollers on the vessel deck after the foam is saturated with oil.

2.1.2 Dynaflow Oil Flotation System

Bubblers have been proposed, prototyped, and occasionally employed in oil spill response for decades to contain and divert oil at the surface. They have also been proposed for subsurface diversion. The diversion mechanism is the current created by the upwelling bubbles at the surface to oppose the spreading and drift

of the oil. They are most likely to be successful in shallow water, confined areas, and in calm conditions to contain, exclude or divert oil from key resources such as water intakes both at and below the surface. The concept of having the air bubbles themselves adhere to individual oil droplets in the water column and transport them to the surface is new.

There is no publicly available information regarding the use of this type of technology for removing the oil from the water column. However, there is information about the effect of natural gas bubbles assisting oil droplets to rise to the surface faster during a blowout. For example, Johansen et al. (2003) note that rising gas bubbles enhanced the rise of oil droplets during a simulated oil and gas blowout in deep water.

2.2 Argonne National Laboratory Adsorbent Foam

ANL proposes to use polyurethane foam, a commonly used material for many general purposes, as the material of choice to adsorb submerged oil. Prior to use, the foam undergoes a series of chemical processes in order to render it oleophilic and thus more susceptible to adsorbing and retaining oil droplets and dissolved oil in the water column.

2.2.1 Envisioned System Operation

The adsorbent foam used for Phase II-A experiments is a 1-inch cube, but during an actual oil spill response scenario, the foam is envisioned to be long strands either integrated with the trawl net itself or contained in several nylon-mesh bags that are tied to a trawl net. As the trawl net is lowered to the appropriate depth and dragged through a submerged oil plume, the treated foam will adsorb the oil droplets and dissolved oil (Darling, 2016). Through typical trawling operations, it can be winched to the surface where the oil will be squeezed out of the foam using compression rollers positioned on the vessel's deck. The foam will be designed to be reused for a number of times without experiencing severe performance degradation. Figure 1 is an example of how the foam may be used in a typical oil spill response scenario.

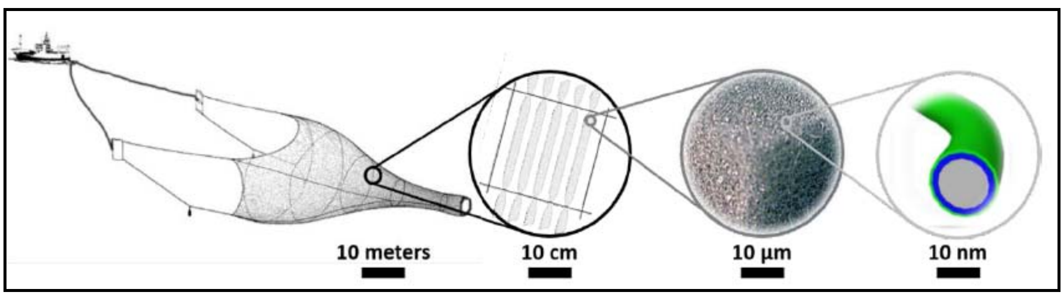

Figure 1. Schematic of foam integrated with trawl net.

2.2.2 Technical Approach

The polyurethane foam is made oleophilic through a patented two-step process. In the first step consists of the sequential infiltration synthesis (SIS) process. In this step, the lining of the voids within the foam are alternately exposed to the precursors, trimethyl aluminum (TMA) and water vapor. This process grows material on the foam to preserve the foam's mechanical properties and prepare it for the next step, which is the coating of an ultrathin oleophilic chemical through the atomic layer deposition (ALD) process (Darling, 2016).

ALD is similar to SIS but involves less exposure time as the process uses silane to coat the surface with a single-molecule-thick film. It does not diffuse into the foam's porous network like the precursors in the SIS process do. Oxidizers such as water or ozone act as precursors during the ALD process and alternating cycles between oxidizers and silane build up the coating on the foam's surface. The two-step process results in a polyurethane foam that is made highly oleophilic and early experiments indicate that a 1-inch cube of the material is able to adsorb oil up to thirty times its weight (Darling, 2016). Figure 2 depicts the two-step process that renders polyurethane foam into an oil adsorbent foam.

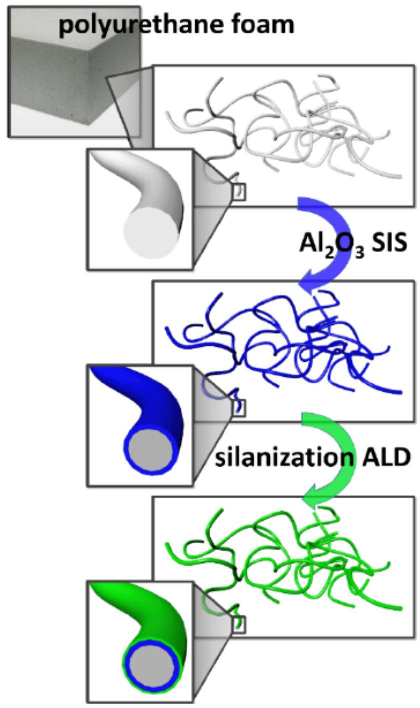

Figure 2. Schematic of two-step process to produce an oleophilic material.

2.2.3 Phase II-A Results

During Phase II-A experiments, ANL used three different types of oil: silicone oil, vacuum pump oil, and Anadarko crude. Experiments testing the performance of treated foams with fresh water were performed with distilled water and most experiments were performed at room temperature of approximately 23 degree Celsius. To determine the recovery capacity, ANL followed American Society for Testing and Materials (ASTM) F726-12, Standard Test Method for Sorbent Performance of Adsorbents (Darling, 2016). It describes the performance of adsorbents in removing non-emulsified oils and other floating, immiscible liquids from the surface of water. The ASTM standard involves several minutes of exposure to oil or water in each experiment. However, ANL did not use the minimum foam mass of 4 grams, which would have required larger cube dimensions and made it more difficult to experiment with in a laboratory setting. Since results are obtained from testing a small foam mass, it is noted that the performance of a larger foam size may be skewed since an exact linear relationship may not be followed. Figure 3 shows the adsorption capacity of functionalized and untreated foams with vacuum pump and Anadarko crude oils over time. It can be observed that oil uptake occurs almost instantaneously for functionalized foams. For each experiment, pure oil was used with the treated foam without the introduction of fresh or salt water.

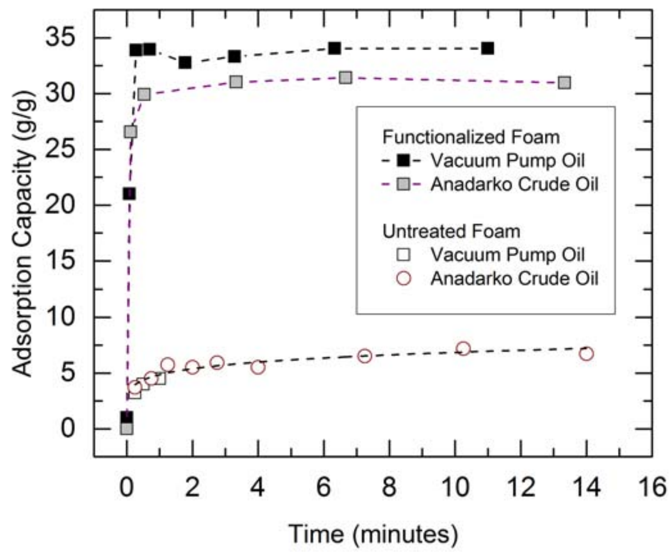

Figure 3. Adsorption capacity vs. time for untreated and treated foams.

Figure 4 shows the adsorption capacity of water and the other three types of oil (without water) for functionalized and untreated foams. Pure oil was again used without being mixed into water. However, for one trial run using a container of only distilled water, it is shown that untreated polyurethane foam adsorbed slightly more water than oil when compared with functionalized foam (see far left of Figure 4). When different pure oils were used, the functionalized foam outperformed the untreated foam by a large margin as seen in Figure 4.

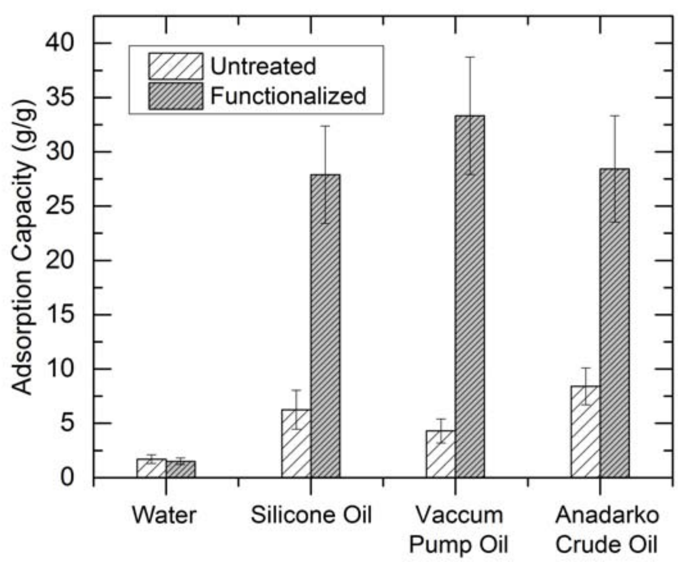

Figure 4. Adsorption capacity of untreated and treated foams with water and different oil types.

The functionalized foam adsorbed approximately 28 grams (g) of Anadarko crude per gram of the foam compared to 8 g of the same oil per gram of the foam when untreated foam is used. The functionalized foam tested with vacuum pump oil shows the best result, adsorbing 34 g/g while untreated foam with the same oil adsorbed 4 g/g.

ANL performed another experiment comparing the foam's uptake capacity of oil and water from the same container and noted that a significantly larger amount of vacuum pump oil was adsorbed with functionalized foam than water whereas untreated foam adsorbed more water than oil. Figure 5 demonstrates that the SIS/ALD process is able to increase the oleophilic property of the foam but further study is needed to determine the performance of the foam for adsorbing crude oil. More importantly, Figure 5, when compared to Figure 4, shows that the presence of fresh water reduces sorbent effectiveness of adsorption of vacuum pump oil from ~34 to 1 to ~11 to 1.

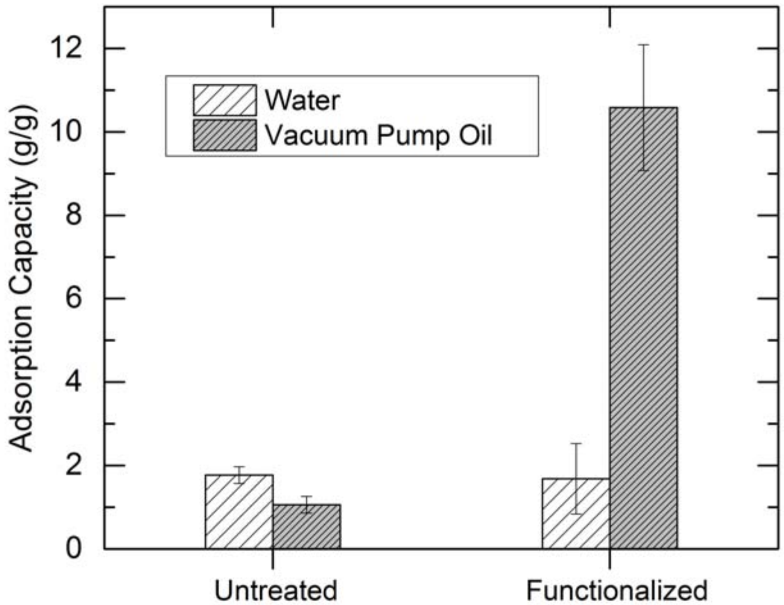

Figure 5. Adsorption capacity of untreated and treated foams with water and vacuum pump oil.

An important property of the foam is its reusability and this is demonstrated in Figure 6. Using vacuum pump oil and functionalized foam, roughly the same amount of oil was taken up by the foam after it was squeezed out by hand. ANL continues to identify the ultimate limits of reusability with this technology (Darling, 2016).

In studying the foam's performance with salt water, Instant Ocean Salt Mix was used to increase the salinity level of the sample water. In an experiment, it was noted that the functionalized foam adsorbed more salt water than oil when Anadarko crude was added to a container of salt water. This is shown in Figure 7. ANL continues to study the interaction of the foam's properties with salt water and it is not currently clear why the functionalized foam performs better in distilled water than salt water (Darling, 2016).

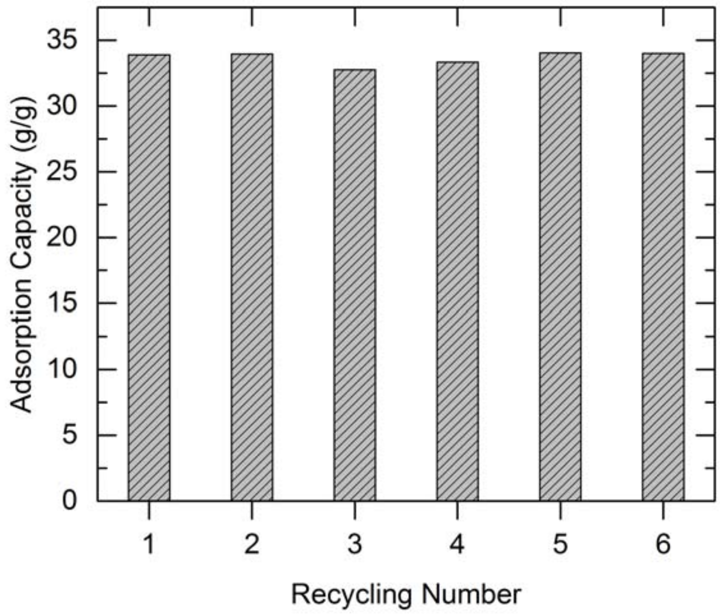

Figure 6. Oil adsorption capacity of vacuum pump oil following compression.

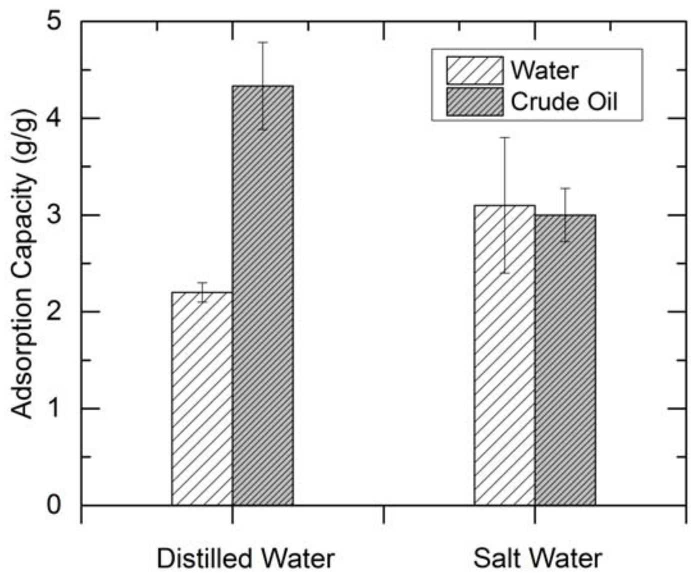

Figure 7. Salinity effect on Anadarko crude adsorption with treated foam.

2.2.4 ANL Phase II-A Summary

Table 1 summarizes the adsorption results for the laboratory tests of the treated foam with oil.

Laboratory testing showed:

- Oleophilic properties of the sorbent material were enhanced by the SIS/ALD functionalization process.
- Effectiveness in pure oil is ~ 30/1.

- Presence of distilled water decreases sorbent effectiveness to ~ 11/1 or less depending on the oil type.
- Sorbent is less effective in salt water than fresh.
- It appears that the material is highly reusable.

Table 1. Treated foam adsorption (in grams oil/grams foam) summary.

	Oil Type		
	Silicone	Vacuum Pump Oil	Anadarko Crude
Oil Only	28	33	28
Oil on Distilled Water	no data	11	4.5
Oil on Salt Water	no data	no data	3

2.2.5 Further Development

Further material development is needed to improve its effectiveness in salt water. The current foam is able to adsorb oil approximately thirty times its weight from a pure oil source and up to about ten times its weight in a distilled water and oil mixture with the oil on the water surface. However, performance is further degraded with the oil floating on salt water. Additionally, the foam will need to be tested for its effectiveness with oil dispersed in the water column in fresh and salt water as opposed to oil floating on the water surface.

ANL will also need to ensure that foam traveling at high speed underwater will not prematurely release oil before it is brought up to the surface and wrung out in an oil container. Prior to re-use, the team will need to ensure that no oil is reintroduced into the water body. This also applies to the wringing operation with rollers, which could potentially be a messy operation, and requires advance planning to reduce contact between oil and responders.

2.2.5.1 Proposed Ohmsett Demonstration Plan

To prepare for prototype demonstration at Ohmsett, ANL will assemble a meter-scale prototype net with the foam. It is anticipated the net will be attached to the moving bridge and towed at a specified depth where the bulk of the submerged oil plume is expected to be. The oil removal efficiency of the foam will be measured by how much oil is collected in a container.

2.2.5.2 Limitations

One of the challenges in a tank environment such as the one located at Ohmsett is to produce a neutrally-buoyant submerged oil plume that can remain in the water column for more than 15 minutes without use of oil dispersants. Additional, effects from the moving bridge and the attached net may have an impact on the oil plume and will need to be accounted for when collecting data.

2.3 Dynaflow Oil Flotation System

Dynaflow, Inc. is developing a mitigation system that utilizes a number of microbubble generators to be placed beneath a submerged oil plume in order to allow air bubbles of differing sizes to adhere and lift oil droplets in the water column to the surface where the oil can be removed by traditional recovery methods.

Dynaflow is also developing fast-running computer software to optimize the position and number of generators and predict the oil recovery location.

The microbubble generator has the capacity to produce very fine (less than 10 µm in diameter) and large (50 to 150 µm in diameter) bubbles simultaneously. The premise of Dynaflow's microbubble generator is that oil droplets in the water column will be adsorbed to the smaller bubbles and the larger bubbles with faster rise time will capture the microbubble-oil mixture and bring it to the surface. Dissolved oil will partition to the gas bubble-water interface due to the hydrophobic nature of the oil. As the dissolved oil concentration increases, the oil will form a separate layer of oil at the interface (Chahine et al., 2016). Combined with traditional oil spill response equipment on the water surface, Dynaflow presents a potentially efficient solution that can mitigate the impact of submerged oil in the water column.

2.3.1 Envisioned System Operation

Dynaflow's oil mitigation solution involves three major components: the microbubble generators, traditional surface oil spill response equipment, and a predictive model to estimate where the bubble-oil mixture would rise. The concept of operations for the oil mitigation system is shown in Figure 8. To assist with monitoring the submerged oil recovery, Dynaflow proposes placing acoustic imaging or other newly developed sensing techniques underwater during an oil recovery operation (Chahine et al., 2016).

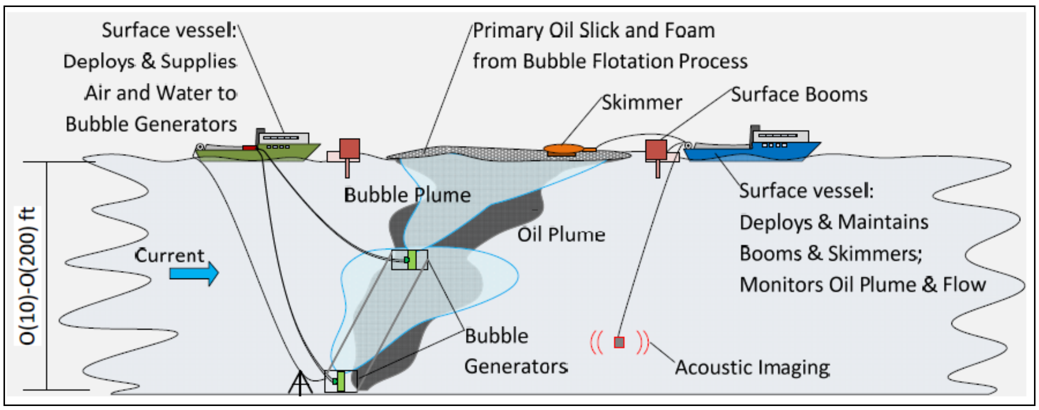

Figure 8. Concept of operations for Dynaflow's oil flotation system.

The predictive model would gather all necessary inputs to predict where the bubble-oil mixture would surface and a boom would be put in the appropriate location to contain the surface oil. Based on preliminary information about the location of the oil plume, a number of generators depending on the estimated plume size will be deployed and turned on, releasing very fine and large bubbles simultaneously.

2.3.2 Technical Approach

Dynaflow's proprietary bubble generator uses the principle of cavitation obtained from specially designed nozzles and bubble shearing to generate very fine bubbles (Chahine et al., 2016). DynaSwirl®, the company's proprietary microbubble generator (Figure 9), was chosen for Phase II-A experiments. It produces cavitation at low pump pressure levels and high flow rates through a swirling flow. Due to the cavitating nature of the jet nozzles, the generator has the capability to produce very fine bubbles and larger bubbles at the same time (Chahine et al., 2016).

Figure 9. Bubble generation by the DynaSwirl® bubble generator.

During Phase II-A, Dynaflow performed several experiments with vegetable oil, Anadarko crude, and Alaska North Slope (ANS) pipeline blend in its plexiglass cube tank measured at 6 ft (1.8 m) x 6 ft x 6 ft. 1,350 gallons (gal) (5,110 liters (L)) of water at room temperature (65-85 °F or 18-29 °C) was used for all experiments. Fresh water and salt water (salinity level at 35 parts per thousand (ppt)) were used to determine the effectiveness of microbubbles on the oil droplets in the water column. Prior to release into the test tank, oil was added into the 55-gal drum through a DynaSwirl® nozzle in order to disperse and emulsify the oil (Chahine et al., 2016). The oil-water mixture was then released into the tank from the bottom through a 1/8" orifice nozzle (see Figure 10).

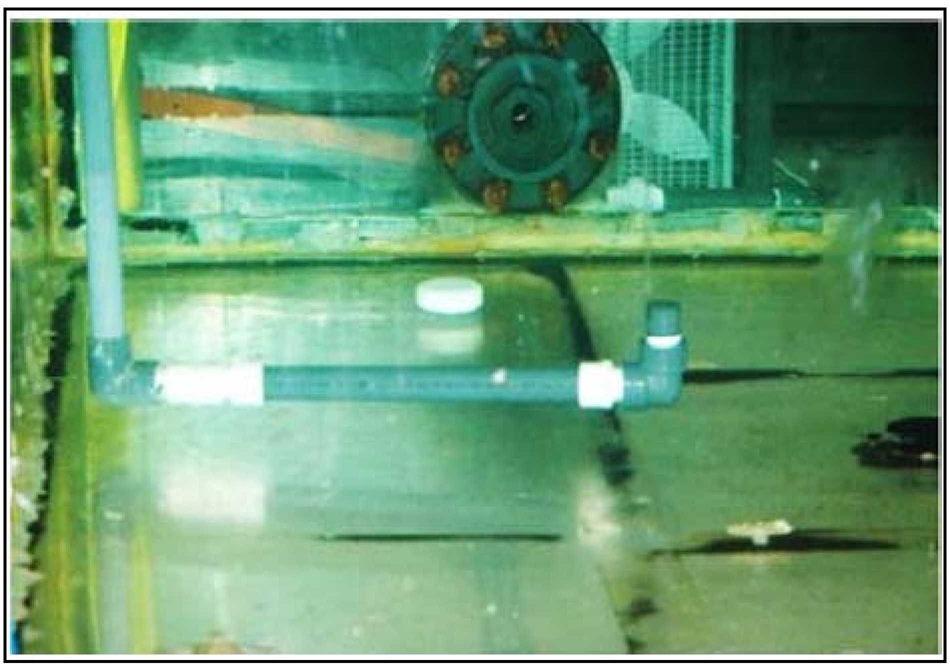

Figure 10. Orifice nozzle for oil release in the plexiglass cube test tank.

For each experiment, the concentration of oil in the 55-gal drum ranged from 2.5 to 4 g/L (Chahine et al., 2016). Approximately 5 to 10 gal (19 to 38 L) of oily water was dispersed into the test tank prior to turning on the microbubble generators to begin an experiment. The oil droplets were created by the cavitating jet method and their sizes were measured using high speed video and image analysis. The sizes of the oil droplets produced were similar to that found in the low end of the *SS Arrow* spill (see Figure 11). Oil release

into the tank lasted approximately 15 minutes before commencement of each experiment. After every experiment, the oily water was filtered using a bank of oil removal filters followed by sand filtration until the water clarity in the test tank returned to what it was before the oil was added (Chahine et al., 2016).

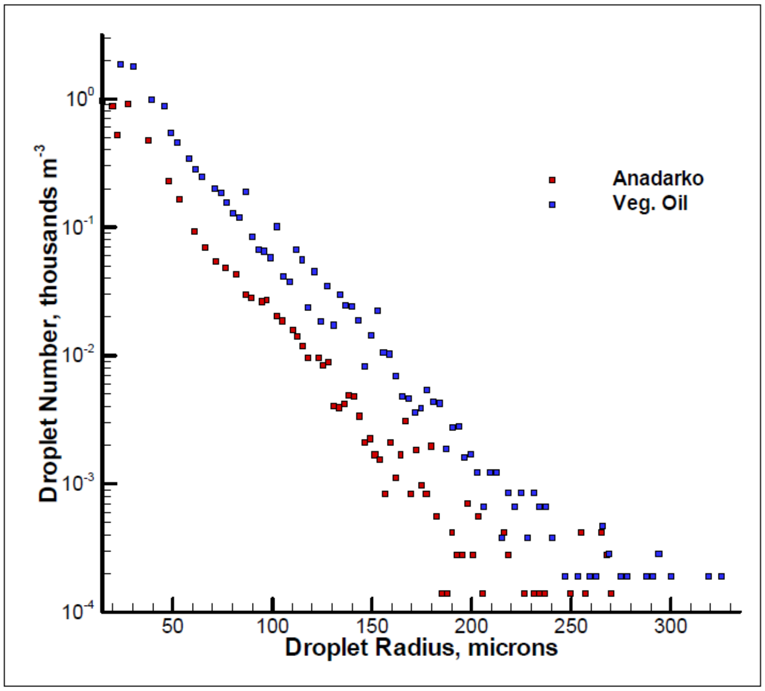

Figure 11. Oil droplet size distribution.

Two bubble generators were used during Phase II-A, placed at the bottom of the tank close to each other in the center near the oil release nozzle (see Figure 12). To minimize the bubble segregation effects due to size differences, the microbubble generator nozzles were oriented downward into a short cylinder so that the bubble cloud would be redirected upwards (Chahine et al., 2016). This led to better removal as the bubble flow had to do a 180 degree turn after release, which slowed down the overall water flow by eliminating the increased upward velocity of the bubble plume due to the initial exit of the air from the nozzle under pressure. This setup allowed the microbubbles to rise due to the effects of buoyancy instead of the pressure from the nozzle and this also increased the contact time between the microbubbles and oil droplets.

A tube oil skimmer was used in the cube tank to recover the oil. Approximately 16 ft (4.9 m) of the tube was placed on the water surface and a mechanism was used to move the tube back and forth across the tank surface to increase contact with oil (see Figure 13). It works by sliding continuously along the tube axis through rollers controlled by a motor. During the recovery process, it picks up oil and is pulled across the water surface and over a series of scrapers that remove oil from the tube. The oil is routed to a stainless steel hopper (Chahine et al., 2016).

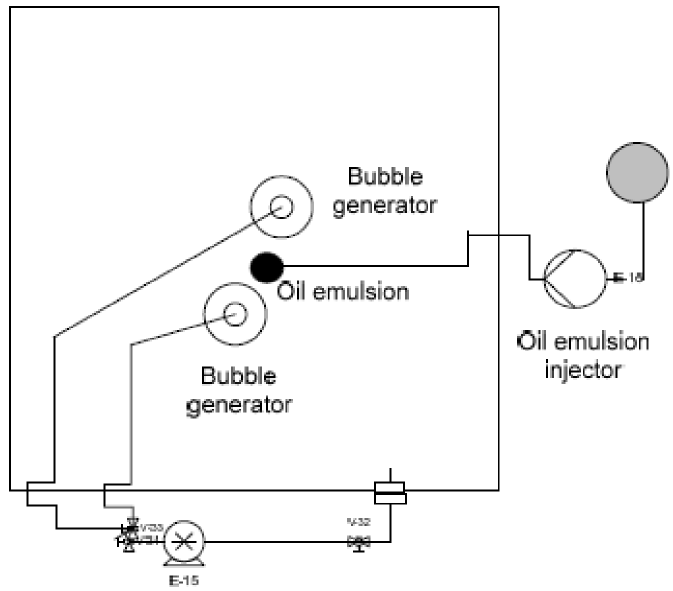

Figure 12. Top view of system setup in the plexiglass cube test tank.

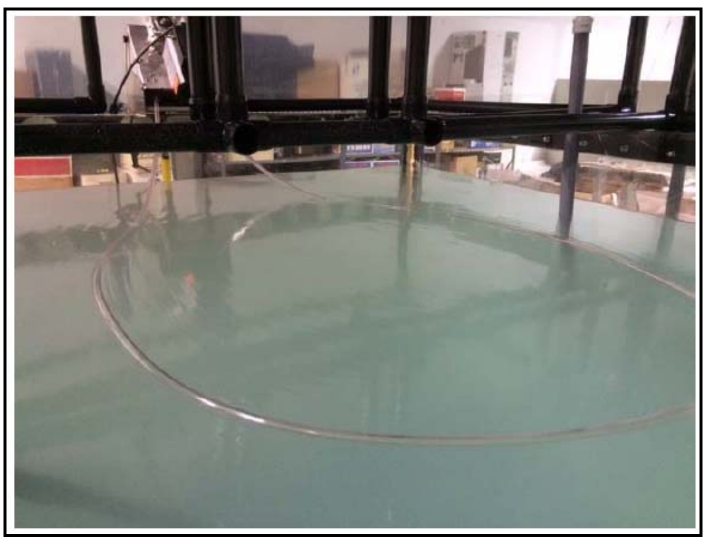

Figure 13. Tube skimmer on the water surface in the plexiglass cube test tank.

2.3.3 Phase II-A Results

In producing air bubbles, Dynaflow noted that injecting air into the low pressure line upstream of the pump so that mixed air and water entered the DynaSwirl® nozzle produced a larger number of small sized bubbles than what was produced from the injection of air into the core of the swirl chamber of the generator (Chahine et al., 2016). Bubble size distributions and concentrations of air were measured using an optical photography method. Dynaflow used a MotionPro IDT Y3 camera and images were processed using the image analysis software, ImageJ, developed by the National Institute of Health (Chahine et al., 2016). Figure 14 shows a greater number of bubbles with small radii using the upstream injection (side) and Figure 15 illustrates that large volumes of 50 to 1000 µm radii bubbles were produced in the tank with air

injection rates of 0.16 to 0.32 gallons per minute (gpm) (0.6 to 1.2 L/min). 0.16 gpm corresponds to 1.7 percent voids fraction and 0.32 gpm corresponds to 3.4 percent voids fraction.

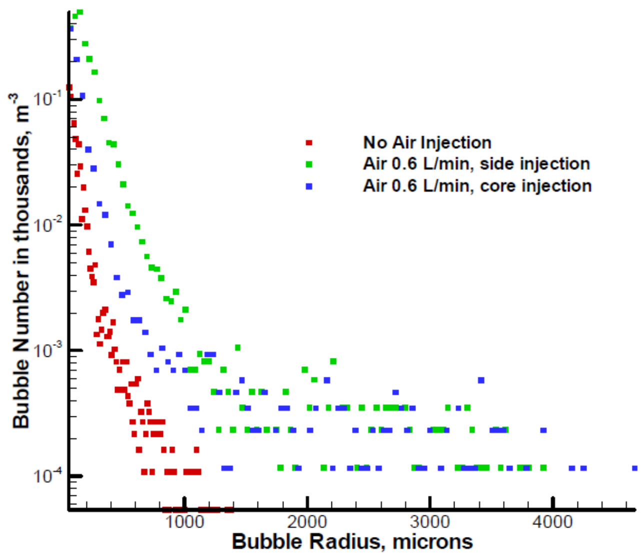

Figure 14. Effect of air injection in the DynaSwirl® nozzle on the bubble size distribution.

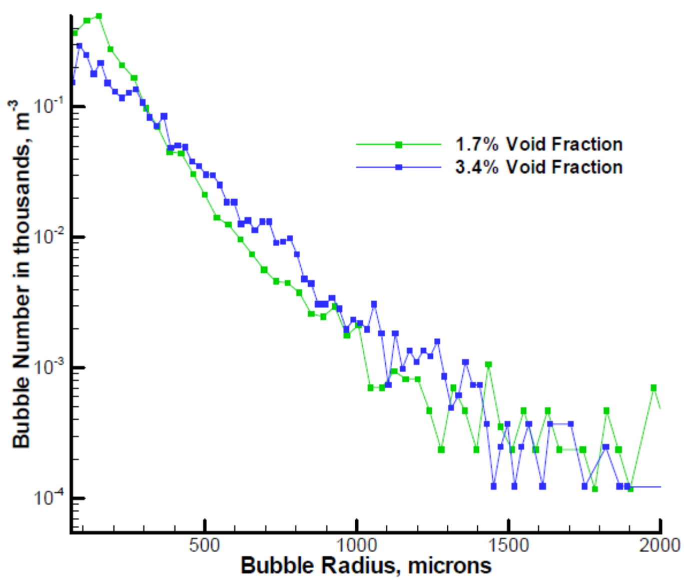

Figure 15. Effect of volume of air injected in the DynaSwirl® nozzle on the bubble size distribution.

From Phase II-A experiments, Dynaflow notes that the bubble radii decreased as the salinity of water increased from 0 to 84 ppt (Chahine et al., 2016). Figure 16 shows a range of approximately 6 to 100 µm of bubble radii produced in all levels of salinity but higher density at smaller radii was observed for waters with higher levels of salinity.

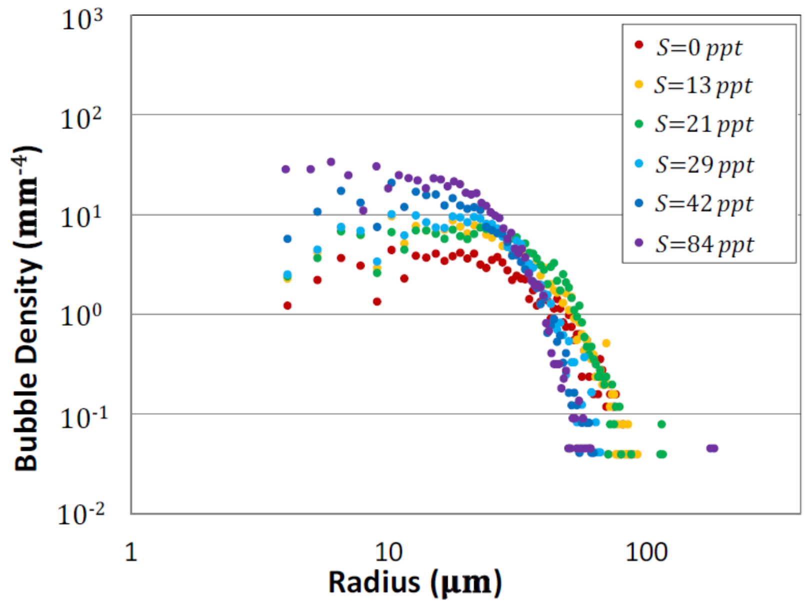

Figure 16. Bubble size distribution for different salinity levels.

This finding indicates that the capture efficiency of the bubbles would be increased in salt water when compared with fresh water due to the presence of smaller bubble radii. When experimenting for oil recovery rates, it was indeed observed that removal rates increased with increased salinity. As Figure 17 shows, most of the Anadarko crude and ANS were recovered after 90 minutes with a removal efficiency of 66 percent for Anadarko and 74 percent for ANS.

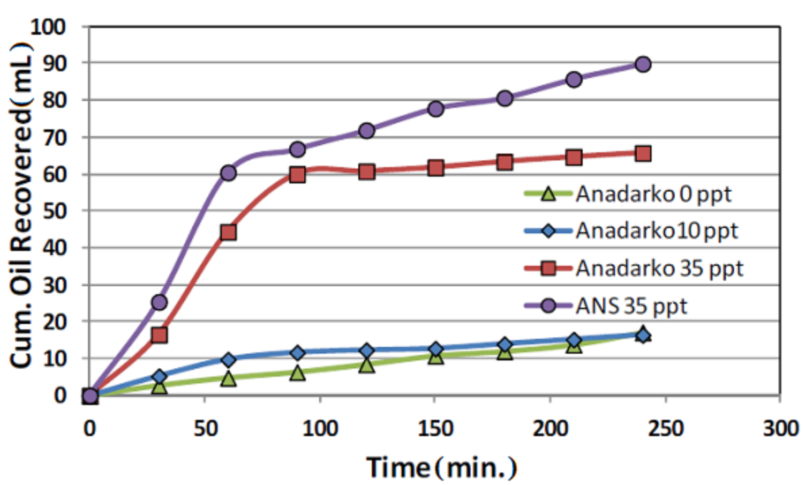

Figure 17. Cumulative oil recovered vs. time for Anadarko and ANS at different salinity levels.

For the next set up, the air injection rate was 0.32 gpm (1.2 L/min) to each bubble generator and air was added for 20 minutes until the bubble generators were shut off. Anadarko crude in fresh water conditions showed the lowest recovery rate, which indicates that salinity has a large impact on the bubble mitigation approach. Figure 18 shows the oil recovery rate of the same experiment documented in Figure 17. It illustrates that the recovery rate rises for a time and then decreases, which may be an indication of the tube skimmer not being able to reach the corners of the cube tank.

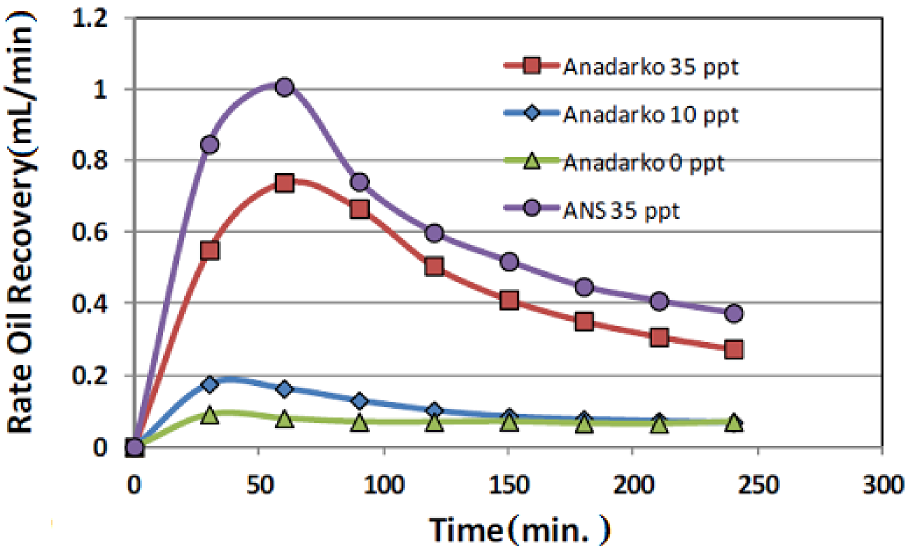

Figure 18. Oil recovery rate vs. time for Anadarko and ANS at different salinity levels.

Dynaflow performed an experiment to compare the cumulative oil recovery to the amount of time. This was performed with and without bubbles. Figure 19 is similar to Figure 17 except data for recovery without air bubbles are shown.

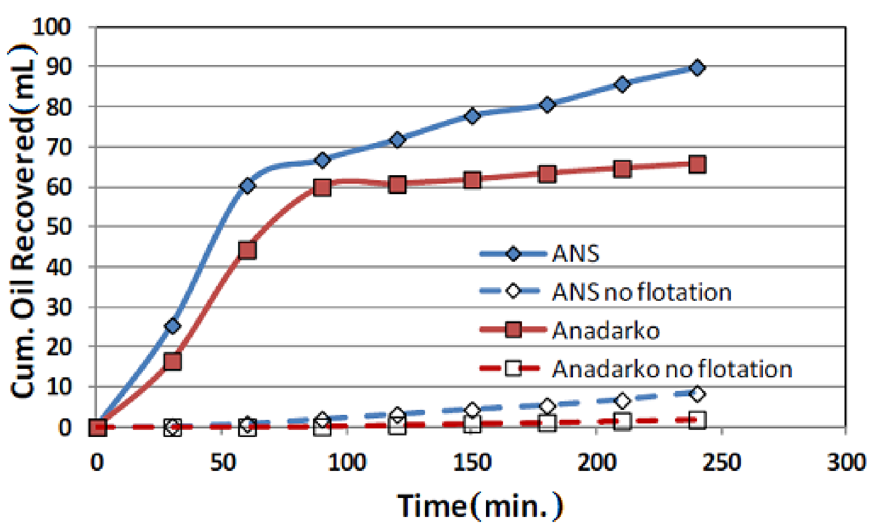

Figure 19. Cumulative oil recovered vs. time for Anadarko and ANS with and without air bubbles.

It can be deduced that without microbubbles, oil droplets take longer times to rise to the surface. At the 90 minute mark, there is much higher cumulative oil recovered for both Anadarko and ANS with microbubbles compared to when there are no bubbles produced (Chahine et al., 2016). Figure 20 shows the terminal velocity of Alaska North Slope crude compared with that of air bubbles over a range of droplet diameters. As the air bubble size increases, its velocity increases as well but the velocity of oil droplets does not increase at the same rate as air bubbles. The natural rise time of oil droplets is much slower than air bubbles

over the same range of diameters, which indicates that air bubbles are effective in speeding up the mitigation process.

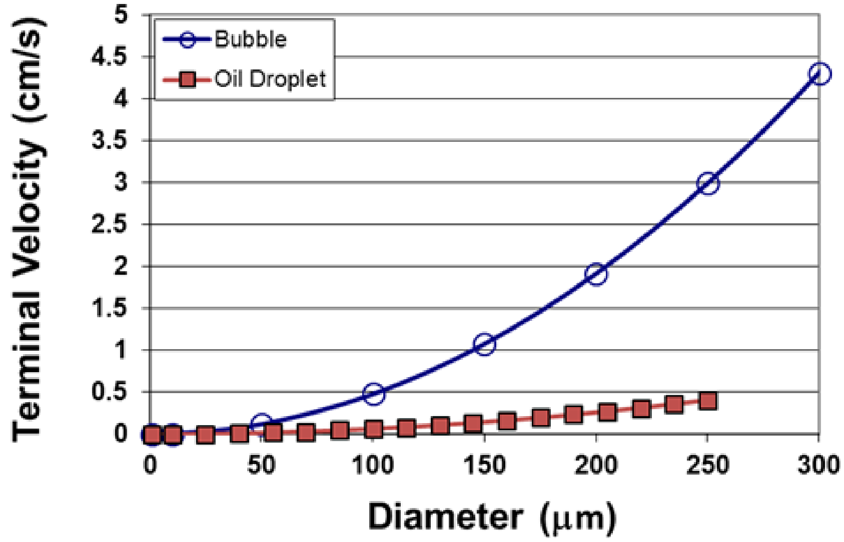

Figure 20. Terminal velocity of air bubbles and Alaska North Slope oil droplets versus droplet diameter.

Studying the effects of current on oil recovery using the microbubbles was attempted during Phase II-A. A centrifugal pump was used to create a 3.5 knot (kt) (5.91 feet per second or 1.8 meters per second) current flow across the top of the tank (see Figure 21).

However, the limitations of the tank prevented a thorough study as most of the oil from the surface was pushed to the tank walls where the tube skimmer could not reach. Also, it is anticipated that oil from the surface may have been pushed back into the tank due to forced recirculation flow in the upper part of the tank.

In parallel with bubble-oil interaction studies, Dynaflow worked on developing a laptop-based fast running simulation software to help plan the oil collection operation. It takes into consideration the terminal velocity and rise time for different bubble sizes. Large bubbles will tend to rise quicker than smaller bubbles due to a number of factors. The inputs to the software include velocity field, oil droplet distribution in space, bubble generator characteristics, location and configuration of bubble generators, and range of errors (Chahine et al., 2016). Outputs include the size and location of the bubble plume and oil droplets. Dynaflow continues to refine the overall model structure and its graphic user interface.

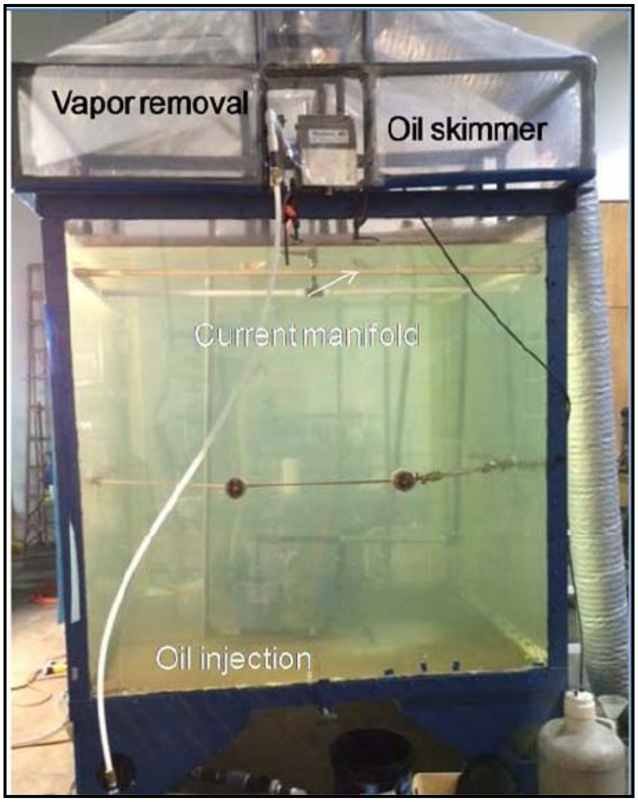

Figure 21. Current manifold in plexiglass cube test tank.

2.3.4 Dynaflow Oil Flotation System Summary

Synopsis of what has been learned:

- Introduction of air bubbles promotes rise of oil to the surface (Figure 19)
- Greater salinity reduces the radii of the air bubbles produced by the system (Figure 16)
- Greater salinity (causing smaller bubbles) increases the recovery of oil at the surface, the inference being that the oil droplets are adhering more effectively to the smaller bubbles (Figure 17 and Figure 18). If the oil droplets were simply being swept upward by the buoyancy of the bubble plume, then the larger radii bubbles should produce greater cumulative oil recovery.

2.3.5 Further Development

Dynaflow's proprietary DynaSwirl® microbubble generator is mature enough to be used for a prototype demonstration at Ohmsett during Phase II-B. However, further modifications to the oil flotation recovery would need to be applied to improve performance in fresh water. The recovery efficiency in fresh water was significantly less than what was observed during operation in salt water. Additionally, the oil skimmer and containment boom would need to be integrated into the oil flotation system approach and its ease of use verified. With this approach, many pieces of equipment will be interfaced with each other to achieve oil mitigation so ease of use and simplicity of operation will be a challenge for the team.

Dynaflow will also need to develop an approach of how the generators may be integrated onto a platform that can be attached to the moving bridge located in the Ohmsett tank.

2.3.5.1 Proposed Ohmsett Demonstration Plan

The team proposes to use at least four microbubble generators at its demonstration in Ohmsett. The oil recovery efficiency of the oil flotation system will be determined with a stationary and moving microbubble generator platform. Once the most efficient bubble generator array is established, the generators will be mounted on a platform, which would be attached to the moving bridge. With a stationary demonstration approach, the platform will remain motionless while a submerged oil plume is generated above it. At the conclusion of the oil release, the generators will be turned on. The differing sizes of air bubbles will adhere to the oil droplets and push them to the surface, where they will be contained by a boom and removed with an oil skimmer. The oil removal efficiency will be recorded with and without the microbubble generators with this stationary approach.

In the moving-platform approach, a stationary submerged oil plume will be produced. After the oil injection, microbubble generators will be turned on and the generator-mounted platform attached to the bridge will move back and forth under the oil plume. Various speeds of the moving bridge will be tested for the best removal efficiency. This would be a simulation of a ship towing the bubble generators through a contaminated region.

The proposed demonstration setup for Dynaflow is amenable to lessons learned during Phase II-B work and feedback from Ohmsett staff.

2.3.5.2 Limitations

One limitation is the same that ANL faces; the ability for a neutrally-buoyant submerged oil plume to remain in the water column for more than 15 minutes without the use of oil dispersants. Oil released in the tank will naturally rise to the water surface due to water circulation in the tank and other factors. Oil recovery data produced by Dynaflow will need to take into account the natural oil particle rise time without microbubbles. This may be overcome with selecting the right combination of pump pressure, oil type, and size of oil-injecting nozzle openings. The wave generator may be utilized. Oil recovery efficiencies with the microbubble generators will need to be compared to those without microbubble generators to determine how much quicker and more efficient the microbubble generators may prove to be.

Another anticipated limitation of the Ohmsett tank would be the challenge of producing a moving submerged oil plume for the microbubble generators to capture. Data may be less accurate in proving how efficient the microbubble generators are in moving water if the generators are themselves moved while the submerged oil plume remains stationary in the test tank instead of the other way around. Another important consideration is to determine the impact of the moving bridge itself on the submerged oil plume.

2.4 Attributes Matrix

Table 2 summarizes how each system meets the BAA attributes.

Table 2. Attributes matrix.

Quality	ANL Adsorbent Foam	Dynaflow Oil Flotation System
1. Extent of oil mitigation or removal rates and quantities	Laboratory experiments indicate maximum adsorption capacity of approximately 30 times its weight with Anadarko crude without water. When tested with Anadarko crude and salt water, adsorption ratio was on the order of 1:1 (water:oil). Adsorption is significantly degraded for oil/water combination.	Microbubbles in plexiglass cube test tank able to remove 66% and 74% Anadarko crude and ANS, respectively in salt water. Experiments were run with 20 minutes bubble time and tube skimmer collected oil for a total of 4 hours. Removal rates slowed after 90 minutes.
2. Types of oil mitigated (e.g., droplets, tarballs, dissolved oil)	Results from Phase II-A indicate adsorption of oil droplets but the foam will not be able to remove tarballs but the net may be able to up to some extent. Recoverable droplet size range needs to be determined. May not remove globules of fresh and/or emulsified oil.	Dynaflow indicates the system has the ability to remove oil droplets but does not mention tarballs. Maximum droplet size affected needs to be determined.
3. Minimization of environmental impacts with a focus on wildlife and plant life	Submersion of the foam into bodies of water should have no adverse impact on the local wildlife or plants. However, trawl net itself may pose risks to mid-water animal species.	Temporary bubble deployments should not have significant impacts on the environment. Introduction of air bubbles into regions of hypoxia during oil spills may be beneficial. Anchors to the water/sea bottom for bubble generators may cause disturbances to the seafloor/river bed.
4. Effective limits in terms of depth of oil and deployment	Phase II-A experiments were performed with pure oil (without water) or oil on water surface in a container. However, ANL indicates foam will be able to function at 200 ft. There are no definitive results that sorbent material can remove (strip out) oil droplets moving in the water column (the problem of interest).	Limit to depth was not tested during Phase II-A but Dynaflow indicates pumps are available to enable effective operations at 200 feet. Depth/pressure effects on bubble size needs to be determined.
5. Effective limits in terms of environmental conditions such as current, wave height, winds, day/night, inclement weather, etc.	Simulated wave testing was performed on a shaker table and harsh repetitive movements with both hands and tweezers. Ability of foam to retain oil during strong winds, waves and currents still needs to be determined. Waves and current may strip oil from material or not allow it to adhere to begin with.	Dynaflow states that wave height and surface winds will not affect bubble technology during operation but surface recovery equipment may not be used in harsh weather. Predictive model may determine where bubble plume will surface but inputs will be needed in a timely manner during a response. Waves and current will increase vertical and horizontal dispersion of bubble plume particularly near the surface. This will decrease air bubble/oil encounter rate and may re-suspend oil that has been floated to the surface. Additionally, extra equipment may be required to monitor currents that would affect plume direction.

Table 2. Attributes matrix (continued).

6. Ease of use to include deployability and recovery of equipment	Traditional trawl net deployment and recovery is straightforward. Oil recovery operation would be considerably less messy on a vessel's deck if foam will not pre-release oil during handling prior to using compression rollers to wring out oil.	Oil flotation system includes multiple, small units that may require anchoring. Overall operation may be complex as many moving pieces require precise coordination during response efforts.Controlling equipment deployment and positioning at depth may be difficult. More likely to be successful in shallow water applications.
7. Transportability	The proposed system (foam and net) would be easily transported from storage to vessel for operations.	Multiple small units are easily transportable but support equipment such as air compressors can be large and difficult to move. All components of spill response operation can be trucked onto site and assembled once aboard vessel.
8. Operability in fresh/seawater	Phase II-A experiments show better performance in fresh water than salt water. The ratio of adsorption for salt water and oil is only 1:1.	Oil flotation system performed better in salt water than fresh water. More information is needed on how the recovery rate may be improved in fresh water.
9. Ability to observe and monitor subsurface oil collection	The system does not include a method to directly monitor oil mitigation. The only available metric is to measure the amount of oil recovered from the foam.	Dynaflow relied on high-speed photography to monitor oil mitigation by the air bubbles in the plexiglass cube test tank during Phase II-A effort. In field applications, the system would be deployed and positioned based on predictive modeling and real-time surveillance.
10. Reusability	Experiments show that 6 cycles of adsorption of vacuum pump oil and compression occurred without significant decrease in performance.	The system contains relatively durable items and they are subject to normal wear and tear, which would require normal inspection and preventative maintenance.
11. Safety to personnel during deploying and recovering	Though the foam materials are not known to be toxic; trawl net operations can be dangerous. Standard safety considerations in deploying and operating spill response equipment at sea.	Multiple pieces of equipment during a response require proper safety procedures and policies. Potential for using high-pressure air to create bubbles at 200 feet may require additional safety equipment and procedures. Standard safety considerations in deploying and operating spill response equipment at sea.

3 OVERALL ASSESSMENT OF PHASE II-B POTENTIAL

3.1 General

Both of these systems are designed for mitigation of the smaller-scale problem of removing suspended oil droplets and dissolved oil from the water column. This type of plume can be generated at Ohmsett, although there may be challenges with keeping the oil suspended in the water column for a sufficient period of time.

3.2 Argonne National Laboratory Adsorbent Foam

Oleophilic (and hydrophobic) materials are routinely used as sorbents during oil spills for oil floating on the surface, suspended in the water column, and stranded on the seafloor. ANL proposes to enhance a specific foam's oleophilic abilities and deploy it in the water column using towed nets. In small-scale laboratory tests, their treated foam was able to adsorb up to 30 times its weight in pure oil and 4 to 11 times (for crude oil and vacuum pump oil respectively) its weight in oil on the surface of fresh water. They were able to demonstrate reusability of the foam at this scale.

3.3 Dynaflow Microbubble Oil Flotation System

Bubbler systems have been recommended and used for surface oil containment and protection of sensitive locations such as water intakes for submerged oil response. In these applications, the pressure of the bubbles pushes the oil away. Dynaflow proposes to inject microbubbles under the oil to transport it to the surface by adhesions to smaller bubbles and entrainment into a stream of larger bubbles. Once the oil is on the surface it can be treated with traditional oil spill response equipment designed for surface oil removal.

Dynaflow's bubble generators were demonstrated in oil removal experiments within a six-foot cube. Nozzle designs, operating conditions such as pumping pressures, air injection rates, number of bubble generators, and their relative positions were tested. The effects of salinity and water current were also tested and it was determined that the oil flotation system performed better in salt water than fresh water. More information is needed on how the recovery rate may be improved in fresh water.

3.4 Summary

Table 3 summarizes the various strengths and limitations of each system discussed above based on Phase II-A findings.

Table 3. Assessment of oil mitigation systems strengths and limitations.

System	Strengths	Limitations
ANL Adsorbent Foam	• Response approach is straightforward and it is able to be used with many types of vessels. • Foam and chemicals used to improve oleophilic properties are non-toxic. • Polyurethane foam is widely available and may be a cost-effective material to use. • Foam is effective in fresh water and laboratory findings indicate it adsorbs approximately five times more oil than fresh water. • Foam is not directly affected by depth of submersion. • Foam may be reused many times without noticeable decrease in performance. • Easy to transport foam from storage to vessel for operation.	• Foam does not perform as well in salt water. Further material improvement is needed. • Does not have the ability to monitor subsurface operation. Effectiveness of foam is measured by oil recovered, which lends to uncertainty in knowing when to stop recovery operations. • Though polyurethane foam itself is abundant and available at low cost, it is unknown if the treatment process will be cost effective. • How will responders know when the foam is saturated and needs to be wrung out? • Trawl nets may be oily and overall response effort may be messy; high likelihood responders will be in contact with oil during recovery operations if foam is oversaturated. • Trawl net may disturb mid-water species. • Oil adsorption rate is limited by oil viscosity and may not recover tarballs. • Working with trawl nets is a dangerous maritime activity. • Maintaining appropriate buoyancy as the foam gains weight from the adsorbed oil may be an issue. • After foam is cleaned from one response, will it be useable at another response? Is there a shelf life?
Dynaflow Oil Flotation System	• Removal rate of oil from the water column is better in salt water than fresh water. • Predictive model may be useful to aid responders in determining where the bubble-oil mixture will surface. • Microbubbles should not harm wildlife, and may help to reduce incidents of hypoxia during an oil spill. • Oil flotation system may be fixed in one location to protect certain sensitive environment areas or manmade structures. • System can be easily moved by a vessel to another region for a drifting oil plume. • System can be scaled up to meet response needs. More bubble generators may be deployed for larger spills but operation complexity may increase. • Pump pressure requirements at 200 feet appears to be low.	• More improvements are needed for recovery of oil in fresh water. • Removal of oil droplets may be feasible with microbubbles but globule or tarball removal may not be possible. Maximum droplet size affected needs to be determined. • Response operation may be complex. Many moving parts will be present at a spill response site, which requires increased coordination among responders during an event. • Microbubble generators may need anchoring, which could disturb seafloor/river bed. • Inputs to predictive model will be needed immediately, which may not be possible in a developing spill response incident. • The pressures in deeper water may affect the size and number of the bubbles generated. • Unclear what type of oil skimmer design would work best with the oil flotation system; to be determined during Phase II-B prototype demonstration.

4 RECOMMENDATIONS

Phase II-A efforts showed that although both technologies face challenges that need to be overcome in order to be a successful oil mitigation option for responders, there were positive findings that warrant further development. Therefore, the RDC recommends that both vendors receive funding to move forward with their work in Phase II-B: Prototype Development and Demonstration.

The following vendor-specific recommendations are made as to the next steps in the development and demonstration process for each system proposed in response to the BAA.

4.1 Argonne National Laboratory Adsorbent Foam

4.1.1 Previous to Ohmsett Demonstration

There are a number of issues that need to be addressed for Phase II-B:

- Compare sorbent effectiveness with a variety of oils in water to the effectiveness of other synthetic sorbent materials on the market (see Table A-1).
- Need to investigate difference between fresh water and salt water performance to determine if this challenge can be overcome.

4.1.2 Demonstration at Ohmsett

The demonstration of the foam in a tank environment should include:

- Investigate in greater detail the effectiveness of material for removing oil suspended in a turbulent, moving water column.
- Develop logistics for deploying the foam-impregnated net in the water column.
- Determine effectiveness of the material integrated into the net.
- Determine reusability.
- Develop prototype test protocol for oil droplet mitigation system (focusing on the concept of oil encounter rate and recovery rate)

4.2 Dynaflow Microbubble Oil Flotation System

4.2.1 Previous to Ohmsett Demonstration

Specific issues that need to be addressed for Phase II-B include:

- Determine optimal bubble size distribution to achieve the greatest oil removal from water column.
- Investigate difference between fresh and salt water performance to determine if this challenge can be overcome.

4.2.2 Demonstration at Ohmsett

A simplified proof-of-concept experiment should be conducted to demonstrate effectiveness in a shallower water application, which is the most likely scenario for use. This would include:

- Use somewhat neutrally buoyant oil and disperse it in the water column at Ohmsett. A wave field may need to be induced to keep it suspended in the water column.
- Allow as much oil to rise to the surface under influence of wave action and buoyancy (without air bubbler system) and sweep with conventional boom and skimmer combination.
- Repeat using the bubbler system and note the difference.
- Keep moving bridge speed slow so as to minimize impact of the bridge itself on the dispersed oil plume.
- Possibly repeat adjusting bubble size to smaller radii.

(This page intentionally left blank.)

5 REFERENCES

5.1 USCG Internal References: Vendor-Specific Design Reports

Chahine, G.L., Loraine, G., Wu, X., Choi, J.-K., and Hsiao, C.-T, "Subsurface Oil Recovery Using Microbubble Flotation", Technical Report, Phase I, Dynaflow, Inc., 2016.

Darling, S.B., "Reusable, Environmentally Benign Absorbent Foams for Oil Spill Pollution Mitigation", Phase I Final Report, Argonne National Laboratory, 2016.

5.2 Additional References

Adams, E.E. and Socolofsky, S.A. (2005). Deep Oil Spill Modeling Activity Supported by the Deepspill JIP and Offshore Operators Committee, December 2004 (revised February 2005).

American Petroleum Institute (API) (2016a). *Sunken Oil Detection and Recovery*, API Technical Report 1154-1, First Edition, February 2016.

American Petroleum Institute (API) (2016b). *Sunken Oil Detection and Recovery Operational Guide*, API Technical Report 1154-2, First Edition, February 2016.

ASMA (2006). *Analyses of Survey, Modeling and Remote Sensing Techniques for Monitoring and Assessment of Environmental Impacts of Submerged Oil During Oil Spill Accidents*. Final report, June 2006.

Brown, H. and Goodman, R.H. (1987). The recovery of spilled heavy oil with fish netting, *1989 International Oil Spill Conference*, American Petroleum Institute, pp. 123–126.

Castle, R.W., Wehrenburg, F., Bartlett, J., and Nuckols, J. (1995). Heavy oil spills: out of sight, out of mind. *1995 International Oil Spill Conference*, American Petroleum Institute, pp. 565–571.

Chapman, N. (2012). *Operational Guidelines on Sunken and Submerged Oil Assessment and Removal Techniques*, International Maritime Organization (2012) draft (in publication).

Coastal Research and Response Center (CRRC) (2006). *Submerged Oil – State of the Practice and Research Needs*, Durham, NH, December 12-13, 2006 (http://www.crrc.unh.edu/workshops/submerged_oil/index.htm).

Daling, P.S., Moldestad, M.Ø., Johansen, Ø., Lewis, A., & Rødal, J. (2003). Norwegian Testing of Emulsion Properties at Sea – the Importance of Oil Type and Release Conditions, *Spill Science & Technology Bulletin,* Vol. 8, Nos. 2, pp. 123-126, 2003.

Deis, D.R., Tavel, N.G., Masciangioli, P., Villoria, C., Jones, M.A., Ortega, G.F., and Lee, G.R. (1997). Orimulsion: research and testing and open water containment and recovery trials, *1997 International Oil Spill Conference*, American Petroleum Institute, pp. 459-467.

Delvigne, G.A.L. 1987. Netting of viscous oils, *1987 International Oil Spill Conference*, American Petroleum Institute, pp. 115–122.

Fingas, M. (editor) (2011). *Oil Spill Science and Technology - Prevention, Response and Cleanup*, Elsevier Inc., Oxford, UK.

Fitzpatrick, M. and Ashburn, O.D. (2011). *Deepwater Horizon Response Submerged and Sunken Oil Symposium*, USCG Research and Development Center, January 2011.

Fitzpatrick, M., Balsley, A., and Hansen, K.A. (2014). *Detection of Oil in Water Column, Final Report: Detection Prototype Tests*, USCG Research and Development Center, July 2014.

Forrester, W.D. (1971). Distribution of suspended oil particles following the grounding of the tanker *Arrow*, *Journal of Marine Research* 29(2): 151-170.

Helland, R.C., Smith, B.L., Hazel, W.E., III, Popa, M., and McCarthy, D.J. (1997). Underwater recovery of submerged oil during a cold weather response, *1997 International Oil Spill Conference*, American Petroleum Institute, pp. 765-772.

Johansen, Ø., Rye, H., Melbye, A.G., Jensen, H.V., Serigstad, B., and Knutsen, T. (2000). DeepSpill JIP– Experimental Discharges of Gas and Oil at Helland Hansen, SINTEF Report, June 2000.

Johansen, Ø., Rye, H., and Cooper, C. (2003). DeepSpill – Field Study of a Simulated Oil and Gas Blowout in Deep Water, *Spill Science & Technology Bulletin,* Vol. 8, Nos. 5–6, pp. 433–443, 2003.

Michel, J. (2006). *Assessment and Recovery of Submerged Oil: current State Analysis*, prepared for US Coast Guard Research and Development Center, June, 2006.

Michel, J. (2008). Spills of Non-Floating Oils – Evaluation of Response Technologies, *2008 International Oil Spill Conference*, American Petroleum Institute, pp. 261-268.

Michel, J., Scholz, D., Henry, C.B., and Benggio, B.L. (1995). Group V Fuel Oils: Source, Behavior, and Response Issues. *Proceedings 1995 International Oil Spill Conference*, American Petroleum Institute.

National Research Council (NRC). (1999). *Spills of Non-Floating Oils: Risk and Response*. National Academy Press, Washington, D.C.

NOAA (National Oceanic and Atmospheric Administration) (1992). *Oil Spill Case Histories, 1967-1991*. Report No. HMRAD 92–11. Seattle, Wash.: Hazardous Materials Response and Assessment Division, NOAA.

Operational Science Advisory Team (OSAT) (2010). *Summary Report for Sub-Sea and Sub-Surface Oil and Dispersant Detection: Sampling and Monitoring*, December 17, 2010.

Ryan, P.B. (1983). Hasbah 6: oil companies response to oil pollution in the Arabian Gulf, *2008 International Oil Spill Conference*, American Petroleum Institute, pp. 371-375.

Schnitz, P.R. and Wolf, M.A. (2001). Nonfloating Oil Spill Response Planning, *2001 International Oil Spill Conference,* American Petroleum Institute, 5 pages.

Sommerville, M., Lunel, T., Bailey, N., Oaland, D., Miles, C., Gunter, P., and Waldhoff, T. (1997). Orimulsion, *1997 International Oil Spill Conference*, American Petroleum Institute, pp. 479-467.

Suzuki, I. and Miki, K. (1987). Research and development of oil spill control devices for use in cold climates in Japan, *1987 International Oil Spill Conference*, American Petroleum Institute, pp 349-358.

Unified Area Command (UAC), Deepwater Horizon MC252 Response (2010). *Strategic Plan for Sub-Sea and Sub-Surface Oil and Dispersant Detection, Sampling, and Monitoring*, November 17, 2010.

Usher, D. (2006). Responding to Submerged Oils in Freshwater Environments, *Freshwater Spills Symposium*, 2006.

van Oudenhoven, J.A.C.M. (1983). The Hasbah 6 (Saudi Arabia) blowout the effects of an international oil spill as experienced in Qatar, *1983 International Oil Spill Conference*, American Petroleum Institute, pp. 381-388.

Wiltshire, G.A. and Corcoran, L. (1991). Response to the *Presidente Rivera* Major Oil Spill, Delaware River, *1991 International Oil Spill Conference*, American Petroleum Institute, pp 253-258.

(This page intentionally left blank.)

APPENDIX A. RESPONSE TO SUBMERGED OIL

Responding to spills of submerged oil is complicated by the problems associated with operating in an underwater environment where oil is spreading and dispersing in three dimensions, visibility is limited, deploying divers is dangerous, and recovery equipment must be far more robust and complex than that used on the surface. Discussions of the various causes, scenarios, type of oils, oil fate and behavior, and response actions are provided in a National Academy of Science Report (NRC, 1999), a later assessment performed for the USCG RDC (Michel, 2006), and a more recently published compilation on *Oil Spill Science and Technology* (Fingas, 2011).

A.1 Submerged Oil Location and Configuration

Submerged oil can be found in three basic forms and sometimes in all three forms in a single spill. The first form to consider is an overwashed oil slick. Overwashed oil occurs in oil slicks located just below the surface where the oil is only slightly positively buoyant so that it is easily covered by water from breaking waves. Although the oil is still readily available for recovery, it is often difficult to detect and map visually from the surface. Airborne surveillance is generally required for monitoring.

Suspended oil is the second form of submerged oil. This occurs where the oil begins to sink from the surface, either because it was negatively buoyant to begin with or has accumulated sediment to increase its density, but reaches a level in the water column where it becomes neutrally buoyant (density of oil approximately equal to that of the surrounding water). This often occurs at a density interface in the water column (pycnocline). The oil will then move at this level with prevailing currents. Often wave action from the surface will help keep the oil entrained below the surface. Detection and tracking of oil in this form is very difficult as it is not visible from the surface and most airborne remote sensing technologies will not penetrate the water column to a significant depth. Recovery is complicated by the poorly defined and often constantly changing location of the oil.

The third form to consider is sunken oil. This is oil that remains negatively buoyant throughout the water column and comes to rest on the bottom. However, even oil that has sunk to the bottom can become intermittently entrained and moved by currents or even roll along the bottom as clumps or droplets. Because this type of oil stays relatively close to the bottom, it can often be detected and mapped by divers and underwater cameras. Some progress has been made in developing in-situ remote sensors to detect and map oil in restricted visibility, at great depth or in other hazardous diving situations. Recovery can often be accomplished by divers and/or underwater suction devices.

In addition to the oil being found at different depths in the water column, it can be found in a range of physical configurations including continuous overwashed slicks; suspended streamers, globules, and finely dispersed droplets; and sunken mats, pockets of oil, and droplets, some of which may be hidden by a thin layer of sediment. Each configuration at any of the three levels in the water column will present a unique set of response challenges. In all three forms, detecting, positively identifying, and mapping the submerged oil is critical to taking effective response actions. These options may include containment or diverting the oil from sensitive resources and infrastructure, closing water intakes, closing shellfish beds and fisheries, subsurface chemical dispersion, and subsurface oil recovery.

A.2 Submerged Oil Scenarios

Submerged oil can result from several scenarios including a damaged vessel at the surface, a sunken vessel on the bottom that is leaking oil, a leaking subsea pipeline, and a subsea blowout. For a damaged vessel or barge leaking on the surface (depicted in Figure A-1, from NRC, 1999), the oil will sink if its density is initially greater than the receiving waters, if it picks up sediment in the water column or by coming in contact with the shoreline or the bottom, and/or is agitated by surface wind and waves. Based on USCG investigations, most of the spills involving submerged oil have occurred from vessels and barges.

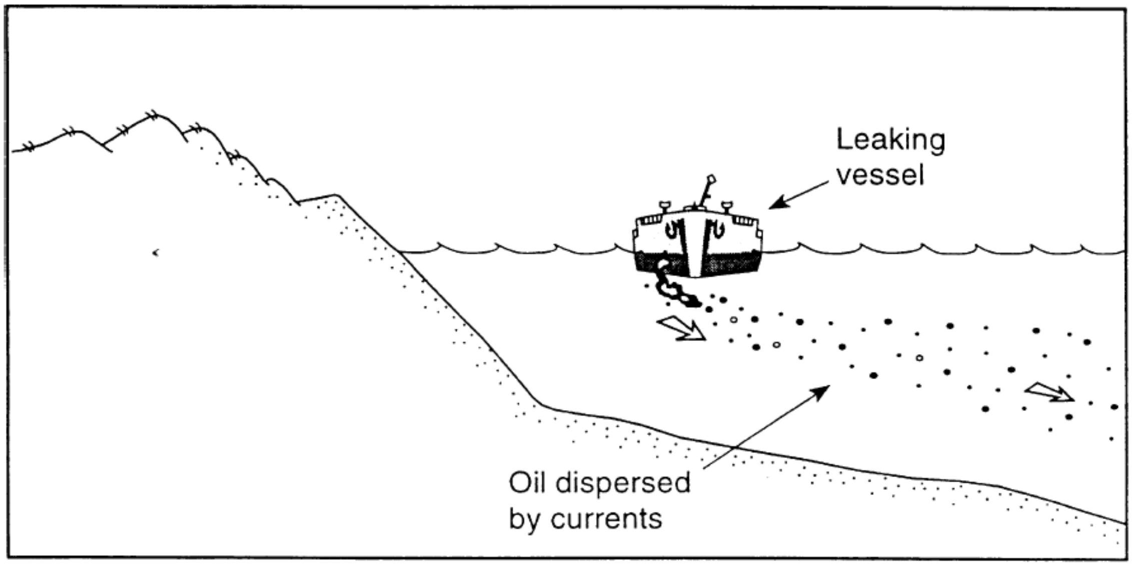

Figure A-1. Heavy oil from a vessel submerged in water column.

The subsea release scenario is depicted in Figure A-2 (from Daling et al., 2003), which shows the oil path for both medium depth (~ 300 ft or 100 m, left) and deep (~ 2,800 ft or 850 m, right) wells. Light oil released from a subsea blowout would be expected to rise to the surface. How fast it rises depends on how large the oil droplets are and the density of the oil. Larger droplets rise faster; small droplets may take months to rise, and very small droplets may never reach the surface. Oil will be transported horizontally with sub-surface currents as it rises. Oil released along the bottom could also accumulate sediment and organic material and be transported with subsea currents at depth.

Oil may be intentionally dispersed in the water column using chemical dispersants to keep it from reaching the surface. This was the case in the Deepwater Horizon spill where much of the oil released remained below the surface as it was transported over great distances. During the Deepwater Horizon response, Figure A-2 was used to illustrate why it was important to apply dispersant at the well head. When dispersants are added to oil (either at the surface or at depth), the surface tension of the oil is reduced and it forms droplets that mix into the water. Dispersants work using the same principles as kitchen detergents. Dispersed oil is not “dissolved,” but the increased surface area to volume ratio allowed naturally occurring bacteria greater access to the oil molecules so that they could be more easily degraded. As with un-dispersed oil, dispersed oil would not necessarily sink unless it was altered by suspended particles or subject to surface agitation.

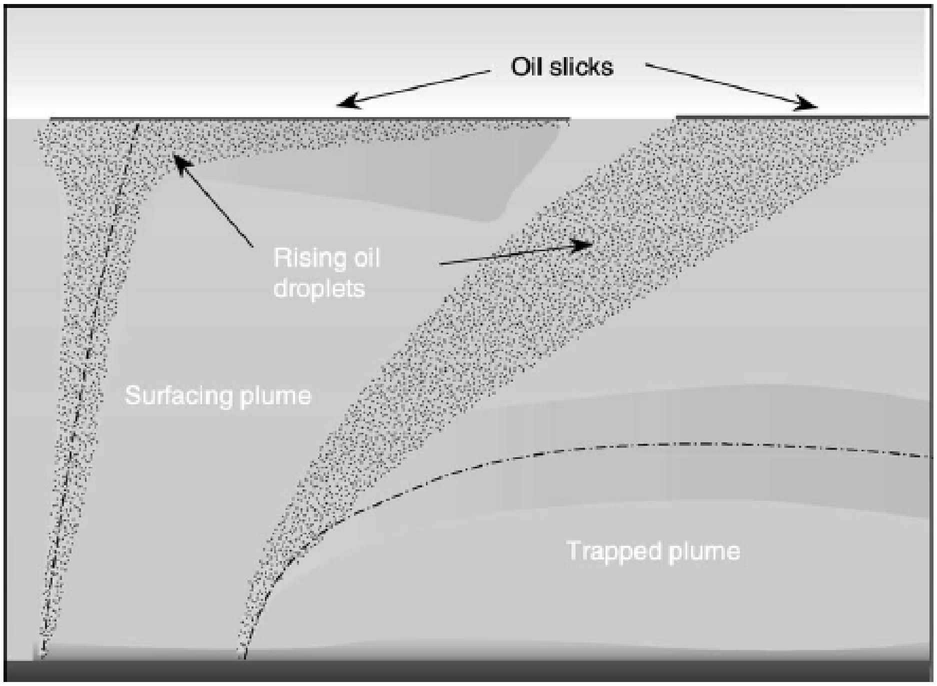

Figure A-2. Schematic drawing of subsea blowouts for medium (left) and deep (right) wells.

Dispersing oil at depth, either naturally or chemically, has the effect of breaking up the oil into small droplets within the water column. Because dispersed oil droplets vary in both size and buoyancy, droplets of different sizes take different lengths of time to rise to the water's surface. Very small droplets, less than about 100 µm in diameter, rise to the surface so slowly that ocean turbulence is likely strong enough to keep them mixed within the water column for at least several months. In the deep ocean, dispersed oil could also encounter "marine snow," a continuous shower of mostly organic detritus falling from the upper layers of the water column (Unified Area Command (UAC), 2010). If subsurface oil is successfully dispersed into small droplets, processes can result in oil remaining in subsurface waters, with horizontal transport potentially many miles beyond the release point.

Smaller amounts of oil may be released from subsea pipeline leaks, or the leaking of oil from tanks after a damaged vessel has sunk to the bottom. Oil arriving at the surface of the water may migrate into the sub-surface again if it is driven into sub-surface layers by wind and wave action (in which case it would refloat when the turbulence subsides), or is altered by encounters with suspended particles.

A.3 Submerged Oil Mitigation

The choice and effectiveness of mitigation technologies is heavily dependent on the condition of the oil suspended in the water column. Most of the technologies recommended in the literature and used in past spills apply to larger fragments of very viscous oil (often termed globules, tarballs, or pancakes). The methods recommended for mitigation of heavy and/or viscous oil include:

- Deep draft oil booms
- Silt curtains

- Sorbents
- Nets and trawls
- Pneumatic barriers
- Manual removal

While there is no readily available information in the literature about mitigation of suspended oil droplets in actual spills, mitigation technologies that may apply include deep draft booms, silt curtains (for larger droplets, we suspect > 1,000 µm), sorbents, and pneumatic barriers (bubblers).

A.3.1 Standard Oil Booms

Deep draft oil booms. Deep draft oil booms (deeper than approximately 4 feet or 1.2 meters) have been considered for containing subsurface oil. In general, standard booms can be used only when the oil remains in the upper water column, the currents are low, and the waves are small. Despite this limitation, conventional booms are commonly applied at heavy oil spills. In fact, booms have been suggested as the preferred option for responding to spills of bitumen-surfactant-water mixtures and have undergone limited testing at sea (Deis et al., 1997; Sommerville et al., 1997). However, these have usually not been deployed intentionally for submerged oil but simply to contain the expected surface slick. Booms can assist in resurfacing submerged oil provided the depth of submergence does not exceed the boom's draft and conventional limitations for boom containment (current speed etc.),. This is particularly the case where weather conditions are a feature of the submergence or overwash, where a thin film of water has gathered on the surface of the oil.

A.3.2 Silt Curtains

*Silt Curtains***.** Silt curtains, which are normally used to control the transport of suspended sediment during dredging operations, are typically restricted to water depths of 10-20 ft (3-6 m) and are deployed so that the bottom of the curtain does not extend to the seabed. Figure A-3 shows a schematic of a Titan silt curtain (left) (www.homeinterior.club/blog/silt-curtain) and a deployed Liquatex silt curtain (right) (liquatex.com.au/product/contractors-silt-curtain/204)

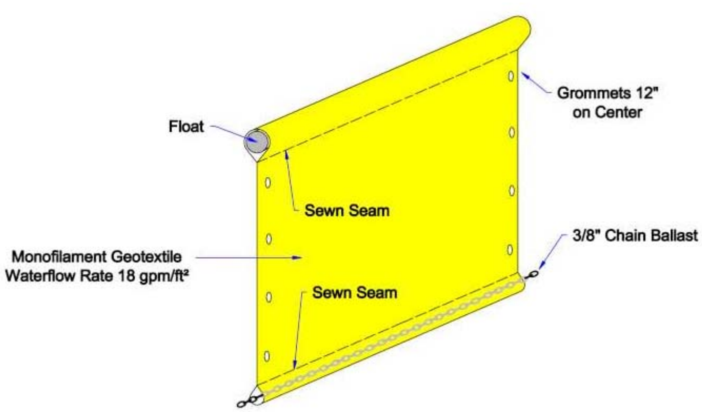

Figure A-3. Silt curtain examples.

A.3.3 Sorbents

Sorbents are insoluble materials or mixtures of materials that recover oil through the mechanisms of absorption or adsorption or both. An adsorbent is an insoluble material that is coated by a liquid on its surface including pores and capillaries without swelling more than 50% in excess liquid. An absorbent is a material that picks up and retains a liquid distributed throughout its molecular structure causing the solid to swell (50% or more). The absorbent is at least 70% insoluble in excess fluid (ASTM designation F726-99).

Sorbents can be natural or synthetic materials. They are available in loose form, which includes granules, powders, chunks, and cubes, often contained in bags, nets, or socks. Sorbets are also available formed into pads, rolls, blankets, and pillows. Formed sorbents are also made into sorbent booms and sweeps. One type of plastic sorbent is formed into flat strips or "pom-poms," which are particularly useful for recovering very heavy oils. Synthetic sorbents can often be reused by squeezing the oil out of them, although extracting small amounts of oil from sorbets is sometimes more expensive than using new sorbent.

The capacity of a sorbent depends on the amount of surface area to which the oil can adhere as well as the type of surface. A fine porous sorbent with many small capillaries has a large amount of surface area and is best for recovering light crude oils or fuels. Sorbents with a coarse surface would be used for cleaning up a heavy crude or Bunker C oil. Pom-poms intended for recovering heavy Bunker or residual oil consist of ribbons of plastic with no capillary structure.

Some sorbets are treated with oleophilic (oil-attracting) and hydrophobic (water-repelling) agents to improve the ability of the material to preferentially absorb oil rather than water. The performance of sorbents is measured in terms of total oil recovery and water pickup. "Oil recovery" is the weight of a particular oil recovered compared to the original weight of the sorbent. The amount of water picked up is also important, with an ideal sorbent not recovering any water. Some results of performance testing of typical synthetic sorbents with various types of oil are given in Table A-1 (Fingas, 2011). The table indicates that all of the tested sorbents pick up water but that more than 90% of the liquid absorbed is oil.

Table A-1. Performance of some synthetic sorbents.

	Typical Oil Recovery with Oil Type (weight:weight)				
Sorbent Type	**Diesel**	**Light Crude**	**Heavy Crude**	**Bunker C**	**Percent Oil**
Polyester pads	7	9	12	20	90+
Polyethylene pads	25	30	35	40	90+
Polyolefin pom-poms	2	2	3	8	90+
Polypropylene pads	6	8	10	13	90+
Polypropylene pom-poms	3	6	6	15	90+
Polyurethane pads	20	30	40	45	90+

Sorbent materials made from plastic in the form of pom-poms, snare nets, and the Vessel-Submerged Oil Recovery System (V-SORS) are often used for detection of submerged viscous oil. They are also recommended as mitigation technologies in some situations (e.g., Schnitz and Wolf, 2001). Figure A-4 shows sorbent pom-poms in a frame used during the Detroit River response in 1996 (Helland et al., 1997). The *M/T Athos 1* response included the V-SORS (Figure A-5) and a snare sampler system (Figure A-6) (Michel, 2006). The V-SORS consisted of an 8-ft carbon steel pipe, 6 to 8 inches in diameter, rigged in a bridle fashion, attached with several 6 to 8 foot lengths of 3/8-inch chain. Around the chains, snare was tied. The system was then towed behind a vessel and dragged along the bottom and somewhat angled through the water column. It was pulled up regularly and inspected for oil. According to ASMA (2006), the V-SORS

was also used for detection and recovery in the *T/B DBL-152* response for oil on the bottom in the Gulf of Mexico.

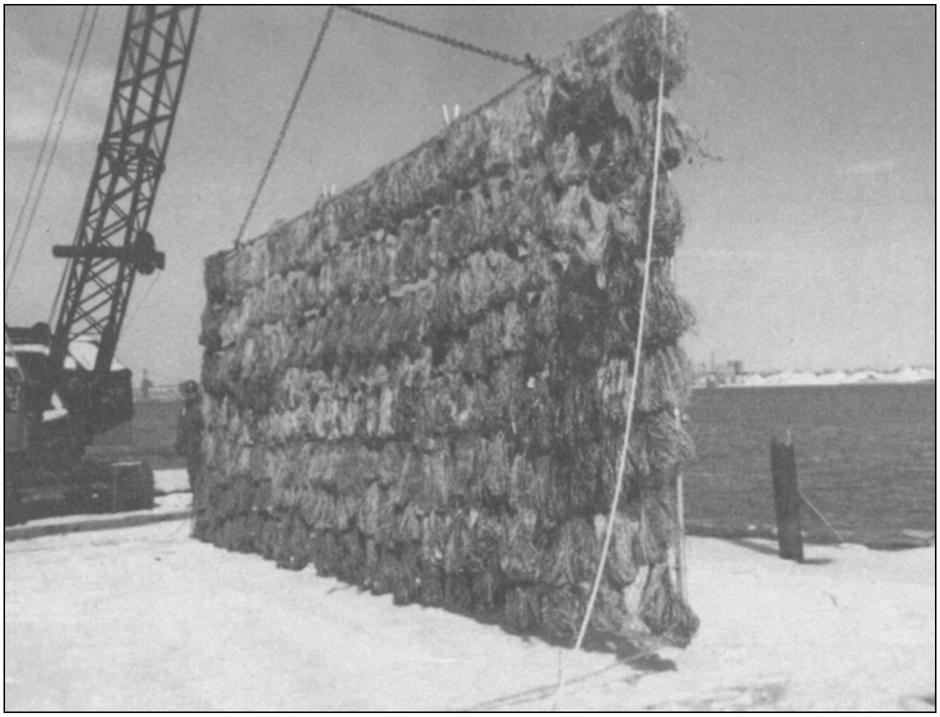

Figure A-4. Sorbent pom-poms from the Detroit River 1996.

Figure A-5. Vessel-Submerged Oil Recovery System.

Figure A-6. Snare sampler system.

Several types of filter fences or curtains made with sorbent materials have been used at spills to either contain oil suspended during recovery of submerged oil from the bottom or to protect water intakes. One such design uses a snare attached to a frame that is suspended downstream of the recovery site (such a design was applied to a coal tar oil spill in the Detroit River where the currents reached 4 knots (Helland et al., 1997)). During the M/T Athos 1 spill, a “snare monster” was constructed out of two frames with snares between them. It was originally built to protect water intakes but was only used to monitor for oil suspension during recovery of oil from the river bottom. In another case, geotextile fabric was used to divert oil from the water intakes at a utility power plant at the Lake Wabamun spill, though there is no information on how well it performed. All of these systems were constructed ad hoc, without the benefit of engineering guidelines on water flow rates, filtration rates, etc.

During a spill in Puerto Rico involving the barge *Morris J. Berman*, strings of snare were tied to lines throughout the water column to recover oil re-suspended during dredging operations. However, success was not recorded as there was no method to measure how much oil bypassed the installation.

A.3.4 Nets and Trawls

Midwater trawls and nets may be used for containing heavy oil in certain conditions. The performance of these systems depends on the viscosity of the oil and being able to locate and concentrate the oil. In addition to containing dispersed oil, nets and trawls can also be used as collection devices (Brown and Goodman, 1987; Delvigne, 1987), and are often combined with sorbents for this purpose.

Specially designed spill recovery trawl nets have evolved in response to the increased carriage and risks of high viscosity oil spills. Such nets lend themselves to recovery of patches of cohesive submerged oils. The principle difficulty with these systems is detection and rapid response to the submerged oil patch such that the trawl system can recover it before it has moved. Fishing nets have not been very successful for recovery of semi solid tarballs; they are likely to be even less effective with more liquid oils.

Delvigne (1987) has suggested that nets can successfully contain oil if the currents are low (less than 10 cm/sec) and the viscosity of the oil is high. Nets can be towed, moored, or mounted on moving floats. This method is sometimes used to protect fixed structures (water intake systems) or resources at risk. The effectiveness of trawls and nets declines rapidly as current speeds increase or as nets become clogged. During the *Presidente Rivera* spill in the Delaware River, fish nets were able to recover eight tons of oil before they became fouled (NOAA, 1992).

In addition to containing dispersed oil, nets and trawls can also be used as collection devices (Brown and Goodman, 1987; Delvigne, 1987). This approach is most successful when the relative velocity of the water and the oil collected in the net or trawl is low and the viscosity of the oil is high. The effectiveness decreases as the permeability of the net is reduced and flows are diverted around the net (Delvigne, 1987).

There are commercially available net booms, though the depth of the net is only 1-2 m below the surface. They are only effective where currents are less than 0.75 knots (NRC, 1999).

The Western Canada Spill Services (WCSS) conducted trials to evaluate the concepts of sunken oil containment. The trials used a fine mesh net and a subsurface containment net. Both systems were deployed using divers but WCSS concluded that in general it was not confident that these were effective for containment or assisted recovery. WCSS is continuing to consider the technique and may conduct further work if new concepts or materials are identified and considered worthy of further study (Chapman, 2012).

A.3.5 Pneumatic Barriers

Pneumatic barriers involve injecting air at the seabed and forming a bubble plume that rises to the surface. They were originally designed to collect and/or divert oil at the surface (Figure A-7 from http://se2mbgreenmarina.blogspot.com/2010/01/science-technology-engineering.html). Pneumatic barriers have been considered for protecting sensitive structures such as seawater intakes and marinas against oil suspended in the water column, and one was used at the Lake Wabamun spill at one of the power plant water intake canals (Fingas, 2011), but little data is available for assessing their performance. Their optimal application is in confined areas in shallow water.

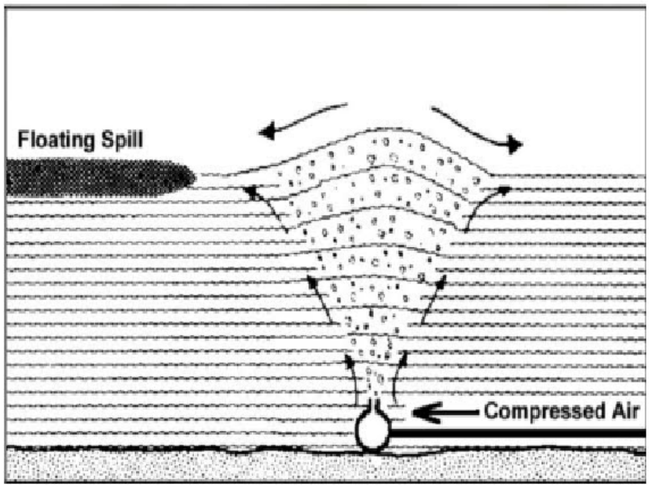

Figure A-7. Pneumatic barrier concept.

A.3.6 Manual Removal

The manual removal of oil, one of the most widely used recovery methods for viscous oil, involves divers or boat-based personnel using dip nets or seines to collect oil, which is temporarily stored in bags or containers. The biggest disadvantages of manual removal are the large manpower and logistical requirements, slow rates of recovery, strong dependency on weather conditions, and the potential for the oil to spread around more when attempting to remove it.

(This page intentionally left blank.)

APPENDIX B. OIL IN THE WATER COLUMN CASE STUDIES

Most well-documented Case Studies relate to sunken oil. There are few experiences with responding to oil in the water column. They do not happen very often but when they do, responders typically take a no-action approach as there are limited efficient technologies that can mitigate the impacts of subsurface oil. Table B-1 lists many of the known cases of suspended oil. The Cases discussed here (shaded in the table) involve detection and monitoring of suspended oil and minimal, if any, mitigation. Note that only two of the incidents involved droplets: *SS Arrow* and *Deepwater Horizon*.

Table B-1. Examples of incidents of oil spills resulting in suspended oil.

Date	Spill Name (reference)	Location	Oil Condition	Water Column Mitigation
1970	*SS Arrow* (Forrester, 1971)	Chedabucto Bay, Nova Scotia	Droplets from natural and possibly chemical dispersion (~100-2,000 µm).	None
1978	*T/V Eleni V* (ASMA, 2006)	England	Huge slicks under the surface.	None
1980	*Hasbah 6 well* (van Oudenhovan, 1983)	Saudi Arabia	Some of the oil was observed to be floating well below the surface.	Conventional fishing nets
1988	*T/B Nestucca* (ASMA, 2006)	Grays Harbor, WA	Tarballs / mats that drifted below the water surface.	None
1989	*T/V Presidente Rivera* (Wiltshire and Cocoran, 1991)	Delaware River, NJ	Large masses in the water column.	One use of fishing net (unable to reuse)
1993	*T/B Bouchard B-155* (ASMA, 2006)	Tampa Bay, FL	Several mats located offshore, 6-20 ft depth.	None
1994	*T/B Morris J. Berman* (ASMA, 2006)	Puerto Rico	Refloating of submerged oil in small globules in shallow waters.	None
1996	Detroit River (Helland et al., 1997)	Detroit River	Mainly on bottom.	Snare barrier
1997	*T/V Nakhodka* (ASMA, 2006)	Honshu, Japan	Heavy fuel oil leaking from the wreck drifted submerged in the water column.	None
1997	*T/V Evoikos* (ASMA, 2006)	Strait of Singapore	Oil slicks fragmented and drifted partially submerged.	None
1999	*T/V Volgoneft 248* (ASMA, 2006)	Sea of Marmara, Turkey	Sunken patches were eventually resuspended due to strong winds, and washed ashore.	None
2002	*T/V Prestige* (ASMA, 2006)	France, Portugal, Spain	Tarballs and emulsion in upper layers.	None
2003	*M/V Fu Shan Hai* (ASMA, 2006)	Baltic Sea	Part of the oil drifted several kilometers below the surface before reaching the sea surface.	None
2004	*M/T Athos 1* (Michel, 2006)	Delaware River, PA	Sunken oil was re-suspended transported by underwater currents.	V-SORS, sorbent barrier/fence
2005	Lake Wabamun (ASMA, 2006; Fingas, 2011)	Alberta, CN	Sunken oil eventually re-floated in the form of small tarballs.	Trawled nets, pneumatic barrier
2005	*T/B DBL-152* (Michel, 2006)	Louisiana	Sunken oil was re-suspended and move above the sediments.	V-SORS
2010	*Deepwater Horizon* (OSAT, 2010)	Gulf of Mexico	Droplets from chemical and possibly natural dispersion.	None

One important aspect that should be borne in mind is that spilled oil that has sunk or been submerged by prevailing sea conditions may not have been observed by the normally-used techniques of visual observation or remote sensing for oil on the sea surface. The spilled oil may therefore have been assumed to have naturally dispersed or dissipated and not be recognized as oil sinking or submerging. In some instances, it has only been the subsequent oiling of shorelines or birds after surveillance has failed to locate the spilled oil that has led to the suggestion that the oil had submerged and then re-surfaced, or had been transported by sub-surface currents. The conclusion could therefore be reasonably drawn that submergence of some types of spilled oils at sea is a more common occurrence than the records suggest, because the consequences are only observed when significant impacts subsequently occur (Chapman, 2012).

B.1 SS Arrow

On February 4, 1970, the 11,397-ton tanker *SS Arrow* ran aground on Cerberus Rock in Chedabucto Bay, Nova Scotia. Almost immediately her 16,000-ton cargo of Bunker C oil began leaking out at an undetermined rate. On February 8 the ship broke in two, and shortly afterward the bow section sank; the stern section rested on the rock until February 12, when it sank also. Some of the cargo was pumped off, but an estimated 9,500 tons of oil leaked into the Bay (Forrester, 1971).

On February 13, the survey vessel *Dawson* was asked to investigate for submerged and sunken oil due to the disappearance of oil from the beach. On February 14, biology technicians conducted subsurface horizontal plankton tows and found small oil particles (~ 100 to 2,000 µm). This began an intensive study of the distribution of these particles in vertical depth, horizontal extent, and size range. The sampling and analytical methods and results can be found in Forrester (1971). No mitigation of the suspended oil was attempted.

B.2 M/T Athos 1

At 9:30 pm on 26 November 2004, the *M/T Athos 1* struck several submerged objects while preparing to dock at the CITGO refinery in Paulsboro, NJ, resulting in two holes in the No. 7 port and center tanks. It was carrying approximately 13 million gallons of Bachaquero Venezuelan crude oil, a heavy crude oil that is heated during transport. The initial report was that 30,000 gallons were released; on 30 November, the volume was increased to a maximum potential of 473,500 gallons. The final estimate of 265,000 gallons released was announced in January 2005 (Michel, 2006).

Although the oil initially floated, there was concern that some of the heavy oil would mix with sediment and not float. Pooled oil was reported on the bottom at the collision site by divers conducting surveys for the submerged objects that holed the vessel. Based on the available observations, it appeared that there were potentially two types of submerged oil: 1) pooled oil that had accumulated in depressions and was not readily mobilized by normal riverine and tidal currents; and 2) mobile oil that was negatively buoyant and subject to transport by riverine and tidal currents.

The mobile oil posed the greatest risk to the many water intakes along the river and bay and shellfish resources in the upper bay. Snare samplers, consisting of an anchor, 15 m of snare on a rope, and a float (shown in Figure A-6), were initially deployed within a few kilometers (km) downstream of the release site to determine where in the water column the oil occurred. These samplers proved effective at providing

qualitative data on the relative amounts of oil suspended in the water column and moving with normal tides and currents.

A second system was developed to both search for and recover the mobile submerged oil, primarily in the accumulation areas on the bottom. The Vessel-Submerged Oil Recovery System (V-SORS) consisted of an 8-ft carbon steel pipe, 6 to 8 inches in diameter, rigged in a bridle fashion, attached with several 6 to 8 foot lengths of 3/8-inch chain (Figure A-5). Around the chains, snare was tied. The system was then towed behind a vessel and dragged along the bottom and somewhat angled through the water column. The chains keep the sorbents along the bottom. The oil readily adhered to the snares underwater. It was pulled up regularly and inspected for oil. The amount of oil recovered was very low, so the V-SORS became more of an assessment tool.

The Salem Nuclear Power plant engineers evaluated different types of sorbent fence or barriers to protect their water intakes from suspended oil, as part of the contingency plan for re-starting the plant. However, no effective designs were identified. The water use at the plant was in the billions of gallons per day, so the design and cost of a barrier would be significant. No threshold was ever established for the allowable amount of oil at the water intakes.

B.3 T/B DBL-152

Shortly before midnight on November 10, 2005, the Tug *Rebel* and Integrated Tank Barge *DBL-152* struck a submerged oil platform that had been damaged by Hurricane Rita about 55 km offshore Cameron, Louisiana. The double-hulled barge was enroute from Houston, Texas to Tampa, Florida. The tug released the barge about 5 km from the platform, once a list in the barge was noticed. The barge drifted for about 15 km until she grounded. Twelve days later, the barge capsized. The *DBL-152* was carrying a heavy refined oil, called a slurry oil, with an API gravity of about 4. The methods by which the oil was blended turned out to be very important to understanding the behavior of the spilled oil. The barge was loaded with oils from five shore tanks that were “line blended” and spread evenly into the bottom of the barge tanks. All tanks were started at one time and the flow and volume from each shore tank was regulated to meet the target specifications of the blended oil. Eventually, it was determined that 2.7 million gallons of oil were released from the *DBL-152* (Michel, 2006).

Because of the density of the oil, it was assumed that most of it would sink, although there was always some floating oil around the barge. It was not until samples were collected from the terminal and the information on the loading methods was obtained that a better understanding of how the oil might behave after release was formulated. The oil sank, but could be readily re-suspended by stirring.

The snare samplers were modified to use “snare-baited” crab pots, replacing the snare strung chain on the bottom to provide a better indicator of subsurface migration of tarballs. These detection systems were called snare sentinels. They were used to detect the spread of the oil over time and provided good indication of how high the oil was suspended during storm events (e.g., in double stacked crab pots, most of the oiling was on the snare in the bottom trap). The biggest disadvantages were the loss rate and the effort needed to deploy/retrieve them over large areas.

The V-SORS required a vessel with a crane or A-frame and winch system to deploy and retrieve the heavy unit, and there were few such vessels available. The vessel had to slow or stop for retrieval, and it took time to get back on station for re-deployment. To address concerns about V-SORS potential snagging and

damaging pipelines, a break-away design was added (weak link on one side) to reduce snagging. To increase the speed of the surveys, an alternative V-SORS design was developed (Figure B-1), called V-SORS (light) consisting of a single bundle of 2-3 chains zip-tied together with snare attached. They could be manually deployed and retrieved, so a V-SORS (L) could be set up on both the port and starboard sides of the vessel. One V-SORS (L) could be dragged on the bottom for the specified distance, and the second one deployed as the first one was retrieved, so there were no gaps in the coverage and no time lost getting back to the waypoint. V-SORS surveys provided consistent data on the spatial extent of submerged oil throughout the response.

Figure B-1. The single chain V-SORS.

B.4 Deepwater Horizon MC252

On April 20, 2010, the Deepwater Horizon MC252 offshore drilling rig situated about 41 miles (66 km) southeast of the Louisiana coast experienced a catastrophic explosion and fire while drilling an exploratory well, killing 11 workers and causing the rig to sink to the seafloor. Two days after the incident, the U.S. Coast Guard announced the leaking of oil from the broken pipe on the seafloor approximately 5,000 feet (~1,500 m) below the surface of the Gulf of Mexico. Additional leaks, coming from kinks in the broken pipe, were observed over the next several days by industry-grade remotely operated vehicles and oil sheen was observed at the sea surface. In the ensuing months, the leak continued nearly three months, making the Deepwater Horizon oil spill the largest in U.S. history.

To reduce the impact of the surface oil reaching sensitive coastal environments, chemical dispersant was applied through surface application and subsurface direct injection into the wellhead. The response to spill included an unprecedented amount of sampling in Gulf of Mexico waters by multiple federal, state, academic entities, and industry (OSAT, 2010).

The National Incident Commander (NIC) was primary interested in assessing the presence of oil that could be removed to prevent, minimize, or mitigate damage to the public health or welfare (also referred to as "actionable oil"). The sampling was conducted in three spatial domains (Figure B-2, figure not to scale): (a) the nearshore from the marshes and beaches (including bays and behind barrier islands) to 3 nm offshore; (b) the offshore, from 3 nm to the shelf break (the ~ 650 ft (200 m) depth contour): and (c) the

deep water, from 650 ft to about 6,500 ft (2,000 m) water depth (the well is in ~ 4,900 ft (1,500 m) of water) (UAC, 2010). The spatial extent of the sampling of shallow waters was guided by previous measurements of the extent of oil at the surface (from ships, aircraft, satellites, and *in situ* sampling) and by knowledge of the nearshore physical oceanography, i.e., movement of water and sediments. Sampling in deep waters was guided by monitoring results obtained to date as well as sub-surface trajectory models.

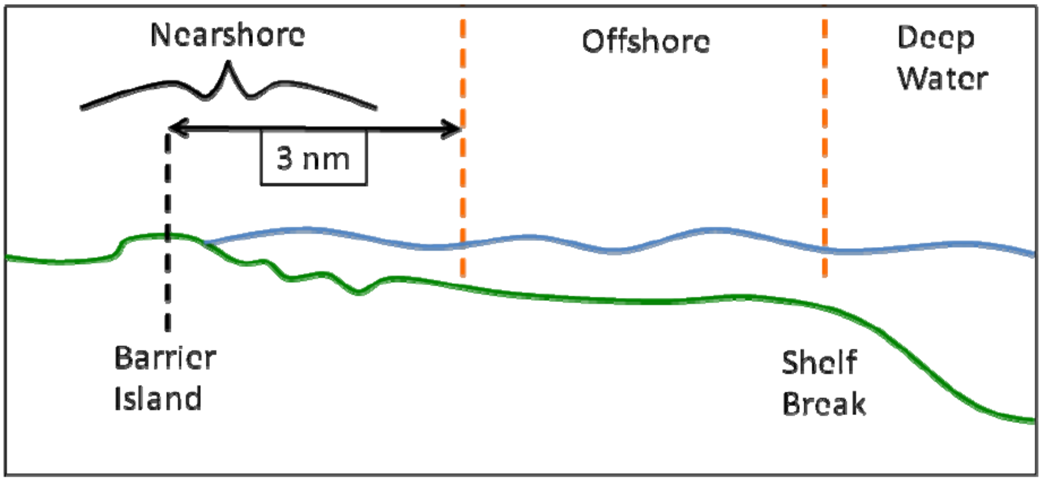

Figure B-2. Spatial domains for sampling.

Detection and sampling techniques and technologies used to determine the location, fate, transport, and threat of oil and dispersants included:

- Snare sentinels, snare drag trawls, and sorbent drops deployed in the nearshore region.
- Collection of water and sediment samples.
- Deep water column
    - Fluorometers
    - Particle size analyzers
    - Oxygen probes
    - Hydrocarbon analyses
    - Standard conductivity, temperature, and depth (CTD) sensor casts.

In the deep water environment, observations defined a diffuse layer of hydrocarbons in the water column, primarily in the 3,300-4,300 ft (~1,000-1,300 m) depth range, that was independently confirmed by a number of sampling teams (UAC, 2010). This oil was not considered actionable and no mitigation of this form of the oil was attempted.

(This page intentionally left blank.)